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Québec Region

EFFECTS OF ACID PRECIPITATION ON A BOREAL FOREST ECOSYSTEM:

ION BUDGETS AND CHANGES IN WATER CHEMISTRY FOR THE LAFLAMME LAKE WATERSHED.

Canada

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by
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ABSTRACT

During the last five years, qualitative and quantitative data on surface waters have been gathered at the Laflamme Lake Watershed in the Laurentide Reserve, Québec, as part of the ion budget program. This federal calibrated watershed was set up in 1980 to assess the effects of long range transport of airborne pollutants on a boreal forest ecosystem receiving moderate to high sulphate loading.

Precipitation data indicates that between 1981 and 1984, the average pH of water falling onto the watershed was of 4,4, that precipitation quality is cyclic and that loading is episodic. The main components of precipitation on an equivalent basis are sulphate, hydrogen, nitrate and ammonium ions. Although the sulphate to nitrate ratio is 2:1 on a yearly basis, nitrate ions are more important than sulphates in January. Wet sulphate loading reached 24 kg/ha in 1983.

Since water and pollutants build up in the snowpack, spring melt is a critical period during which concentrations in surface waters and exports from the watershed are modified for many parameters especially hydrogen and bicarbonate ions.

Lake water quality (alkalinity < 200 µeq/l, calcium < 200 µeq/l and conductivity < 30 µS/cm) is characteristic of lakes that are very sensitive to acidification. High sulphate values (> 60 µeq/l) seem to indicate that the watershed has been affected by atmospheric loading. The average pH of the lake (6,4) indicates that the lake is not yet greatly acidified. Important buffering occurs in the soil and surficial deposits of the watershed. Stream water is slightly less mineralized, slightly more acidic and shows more pronounced changes in water quality than lake water.

Over the last five years, sulphate, conductivity and some heavy metal levels have increased in surface waters while no significant trends were seen for pH and alkalinity. In other Quebec monitoring lakes, trends of decreasing pH were seen during this period.

When wet loading is compared to stream output, hydrogen and nitrate ions are seen to be retained in the watershed while calcium, magnesium, sodium, potassium, sulphate and chloride are lost.

RESUME

Depuis cinq ans, l'acquisition de données quantitatives et qualitatives pour l'étude du bilan ionique s'effectue au bassin versant du lac Laflamme dans la réserve des Laurentides, Québec. Ce bassin calibré fédéral a été établi en 1980 pour étudier l'effet du transport à grande distance des polluants atmosphériques sur un écosystème de type boréal soumis à des dépositions moyennes à fortes de sulfates.

Les données de précipitation indiquent que pour la période de 1981 à 1984, le pH moyen de l'eau tombant sur le bassin était de 4,4, que la qualité des précipitations était cyclique et que les dépositions atmosphériques étaient de nature épisodique. Les composantes majeures des précipitations, exprimées en équivalents, sont les sulfates, les nitrates, l'ion hydrogène et l'ion ammonium. Bien que le rapport des sulfates aux nitrates soit de 2:1 sur une base annuelle, les taux de nitrates dépassent ceux des sulfates au mois de janvier. En 1983, les apports humides de sulfates ont atteint 24 kg/ha.

Puisque l'eau et les polluants s'accumulent dans le couvert de neige, la fonte printanière est un temps critique durant lequel les concentrations dans les eaux de surface ainsi que les charges à l'exutoire sont modifiées pour plusieurs paramètres dont surtout les ions hydrogènes et bicarbonates.

La qualité de l'eau du système lacustre (alcalinité < 200 µeq/l, calcium < 200 µeq/l, conductivité < 30 µS/cm) est caractéristique des eaux très sensibles à l'acidification. Les fortes valeurs de sulfates (> 60 µeq/l) semblent indiquer que le bassin est affecté par les apports atmosphériques. Toutefois, le pH moyen du lac (6,4) indique que le lac ne serait pas encore acidifié. Une neutralisation importante a lieu dans les sols et les dépôts meubles du bassin. L'eau à l'exutoire est un peu moins minéralisée, un peu plus acide et subit des changements plus prononcés que l'eau du lac.

Au cours des cinq dernières années, les niveaux de sulfate, de conductivité et de certains métaux traces ont augmenté dans les eaux de surface alors qu'aucune tendance significative n'est apparue pour le pH et l'alcalinité. Dans d'autres lacs du réseau de surveillance au Québec, des diminutions de pH ont été notées pour la même période.

Lorsque les apports humides sont comparés aux charges à l'exutoire, on voit que les ions d'hydrogène et les nitrates sont retenus dans le bassin alors que le calcium, le magnésium, le sodium, le potassium et les ions sulfates et chlorures ont des exportations nettes du système.

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INTRODUCTION

During the last two decades, society has been faced with severe environmental problems related with the production, transport and disposal of dangerous materials. Long range transport of airborne pollutants (LRTAP) is one of the by-products of our industrial age linked mainly with the emission of sulfur dioxide and oxides of nitrogen from smelters, electric utilities, refineries or the transportation sector. Lakes in Eastern Canada are especially susceptible to this type of pollution since a large number of lakes on the Canadian Shield are poorly mineralized and have low acid neutralizing capacities.

Because of this fact, in the province of Quebec, both the provincial and federal governments have set up programs to determine the effects of LRTAP on aquatic systems. While the Province has now concentrated its efforts on a spatial coverage of the extent of acidification (Dupont, 1987), the federal government is more concerned about temporal trends in acidification (Haemmerli, 1986) and integrated monitoring.

Integrated monitoring was established in 1979, at three calibrated watersheds (Turkey Lakes/Ontario, Laflamme Lake/Québec and Kejimkujik/Nova Scotia). A calibrated watershed is a physiographically defined area in which hydrological and chemical inputs, their movements and their interactions with various components in the system, are studied intensively and on a continuous basis. This type of framework is ideal for mass balance studies which are basically budgeting what enters and what leaves the watershed. In order to establish both water and chemical budgets, information must be gathered from many levels in the ecosystem (precipitation, forest canopy, soil, groundwater, streams and lake) as shown in figure 1. With this approach, the quantification of pathways and responses of a boreal watershed to acid deposition can be evaluated, first, by monitoring the impact on lake and outlet water chemistry and, secondly, by looking at the effects on the output of ions from the watershed.

This report deals with data gathered at the Laflamme Lake watershed (LLW) from 1981 to May 1986. Information is given on the site itself, on precipitation data, on watershed water chemistry, on lake and outlet water chemistry as well as on inputs and outputs for the watershed.

OBJECTIVE:

TO UNDERSTAND AND QUANTIFY GEOCHEMICAL RESPONSES OF A WATERSHED TO ACID LOADING AND TO DEFINE CAUSE-EFFECT (LOADING/RESPONSE) RELATIONSHIPS FROM WHICH PREDICTIVE MODELS OF ECOSYSTEM EFFECTS CAN BE DEVELOPED AND VERIFIED.

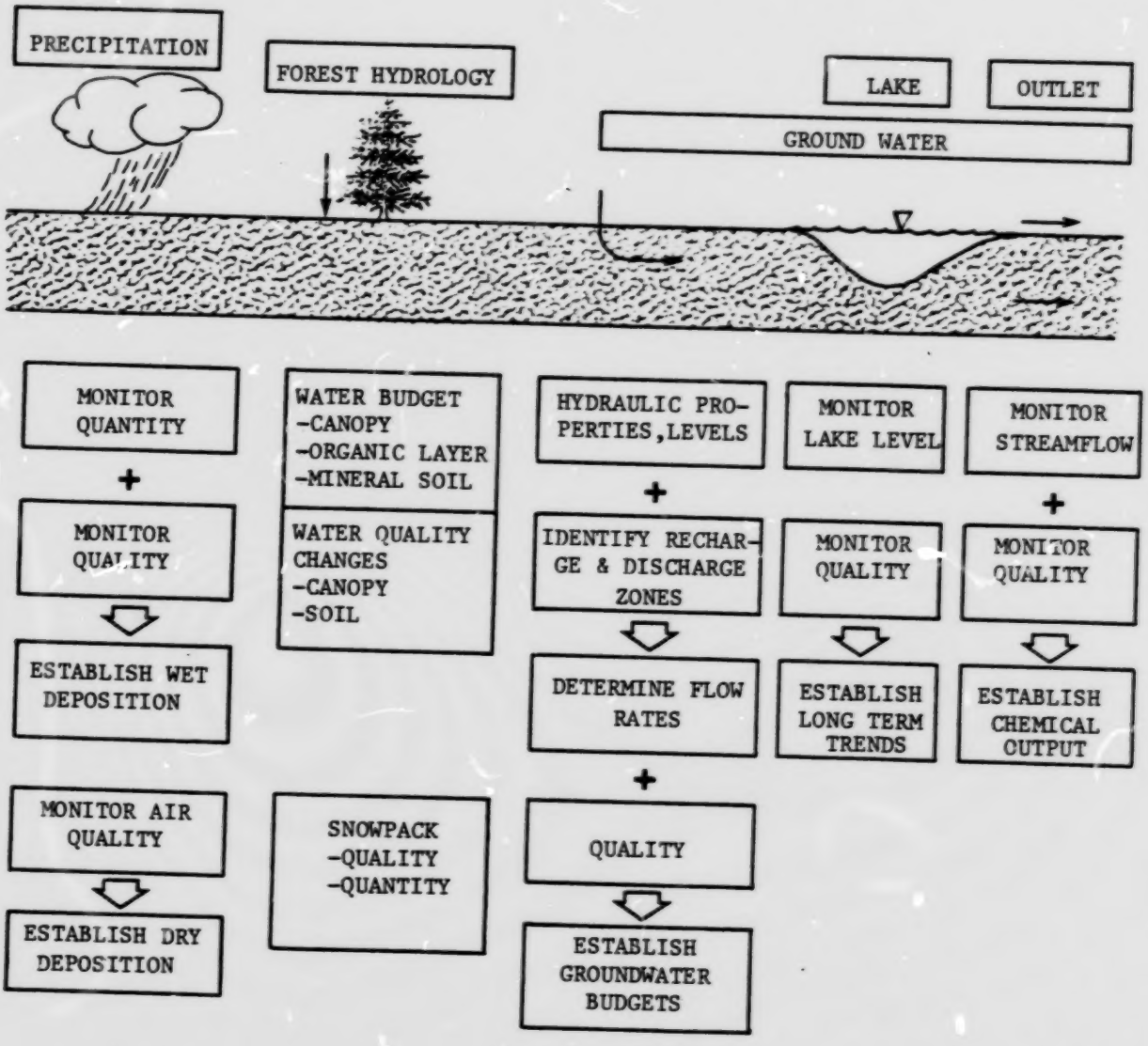

FIGURE 1 : MAIN COMPONENTS OF ION BALANCE STUDY IN LAFLAMME LAKE WATERSHED.

1. SITE DESCRIPTION

The Laflamme Lake watershed (LLW) is part of the 200 000 km^2 boreal balsam fir forest which stretches across Quebec from west to east. The watershed is located on the Laurentian Plateau, an area with a general relief showing no truly contrasting forms and with a gently rolling surface slashed by a number of fractures of regional scale. This headwater lake discharges into the Montmorency River which flows south into the St-Lawrence River east of Quebec City. Main characteristics of LLW are given in table 1.

1.1. Location, Area and Topography

The LLW is located within the Montmorency Forest, an experimental forestry station operated by Laval University, some 80 km north of Quebec City (figure 2). The lake is situated at a latitude of 47° 19' and a longitude of 71° 07'. The altitude ranges from 777 m to 884 m. The watershed covers 68,4 ha of which the lake occupies 6,1 ha. The maximum slope is 30% while the mean slope is 9%. The relief is regular and the northern slope has higher elevations and steeper slopes than the south side of the catchment (Plamondon, 1981) (figure 3).

1.2 Climate

The climate of the area is characterized by low temperatures and abundant precipitation. The summers are short and cool and the winters are long and cold. The majority of air masses flow from west to east so air affecting the LLW is predominantly continental. During the winter months, storms may blow in from the Maritimes.

Annual precipitation averaged 1,3 m from 1981 to 1985 of which 34% fell as snow. A continuous snowpack develops each winter to a height of 1,2 m and disappears in May. Occasionally mild temperatures and rain in midwinter partly melt the snowpack. The lake surface remains frozen from mid-November to mid-May.

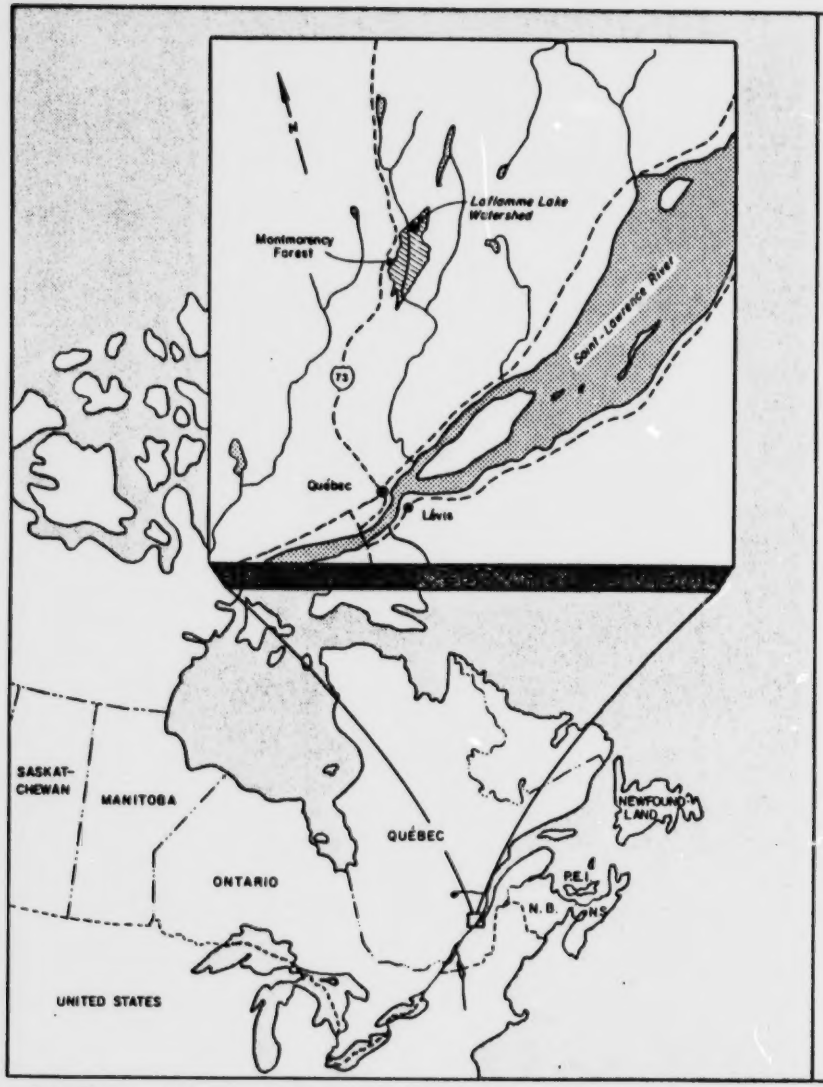

FIGURE 2 : LOCATION MAP OF THE LAFLAMME LAKE WATERSHED.

Table 1. Laflamme Lake Watershed Characteristics.

Latitude	47° 19'
Longitude	71° 07'
Total basin area	0,684 km^2
Altitude (min)	777 m
Altitude (max)	884 m
Slope (min)	0 %
Slope (max)	30%
Mean slope	8,6%
Lake area	0,061 km^2
Lake perimeter	1,02 km
Maximum depth	5,3 m
Mean depth	2,05 m
Lake volume	125 x 10^3 m^3
Bedrock	charnockitic gneiss
Surficial deposits	ground moraine, outwash till
Thickness of deposits	4 m (slope), 15 m (under lake)
Type of soil	orthic humo-ferric podzol
Drainage	good to imperfect
Permeability (deposits)	1,5 x 10^{-3} cm/s
Vegetation	Balsam fir, White spruce, White birch
Macrophytes	Nuphar, Eleocharis, Carex, Sagittaria
Fish population	Brook trout
Lake recharge	Small streams, upswellings, groundwater
Lake discharge	one main outlet
Renewal rate	2 months
Outflow (min)	< 0,001 m^3/s (Jan 9, 1985)
Outflow (max)	0,198 m^3/s (May 1, 1986)
Freeze up	mid-November
Break up	mid-May
Annual precipitation	1,3 m
Montmorency Forest Data	
Air temperature (max)	34° C
Air temperature (min)	-41° C
Air temperature (mean)	0,2° C
Days with frost	234

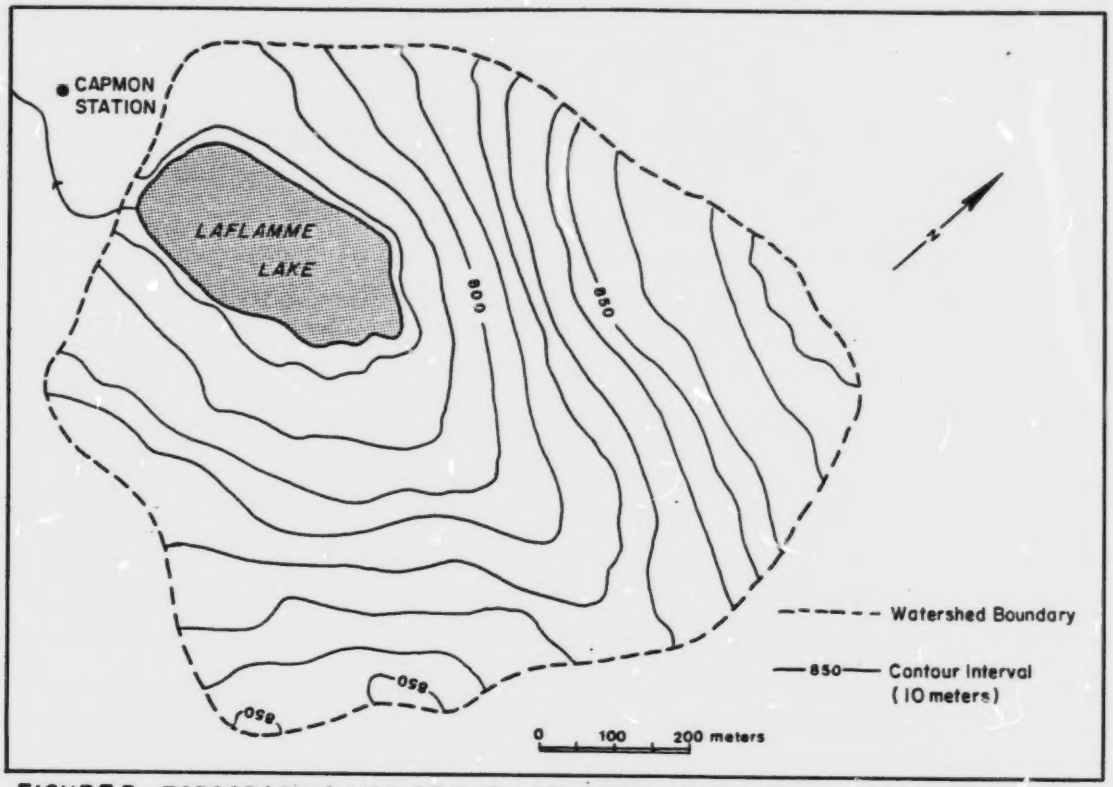

FIGURE 3: TOPOGRAPHIC MAP OF THE LAFLAMME LAKE WATERSHED, ADAPTED FROM PLAMONDON, 1981.

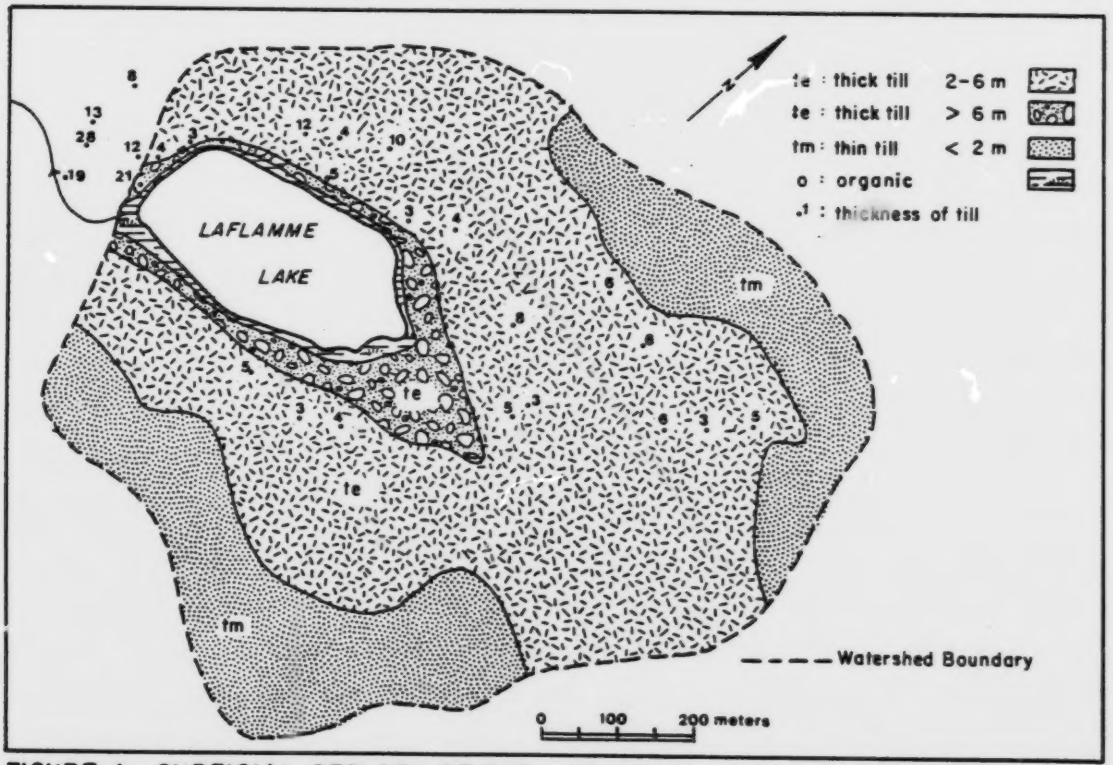

FIGURE 4: SURFICIAL GEOLOGY OF THE LAFLAMME LAKE WATERSHED.

Based on data from the main weather station at the Montmorency Forest for the period of 1966 to 1980, the mean temperature of July was 14,8° C and that of January was -15,2°C. The mean annual number of days with frost is 234. The growing period extends generally over 144 days from mid-May to early October. There is an average of 1 763 hrs of insolation per year. The average wind speed is 7 km/hr.

1.3 Geology

The watershed lies entirely within a very large massif of precambrian charnockitic gneiss of the Grenville geological province. The charnockitic rocks vary in composition from granite to gabbro but mangerite is the more common. The bedrock is not fissured, impermeable and not easily altered. Rock mineral composition is mainly feldspathic with a little quartz and mafic minerals (Azzaria et al., 1982).

Surficial deposits are a mix of locally derived material and material carried in from the north by glaciers. Most surficial deposits are till and moraine composed predominantly of potassic feldspar, quartz and plagioclase (figure 4). The silt and clay fraction is low, the average being 10%. The predominant clay mineral in the surface layer is kaolinite. The till is composed of boulders and cobbles in a sandy matrix. The thickness of the till reaches over 15 m, in an underground valley under the lake (Robitaille et al., 1983a). The average depth in the recharge area is of 4 m which is rather high for the area. The thickness of the till decreases with altitude to about 0,1 m. Few outcrops are present in the watershed. Two swamps cover areas near the lake shore.

1.4 Soils

The soils in the watershed are mainly orthic ferro-humic podzols (figure 5). The well drained soils belong to the Laurentide and the DesNeiges series with moderately drained soils belonging to the Piché and LaFoi series. The gleyed humic podzols are of the Coligan series and are poorly drained (Robitaille, 1983). The well drained podzol of the Laurentide series is

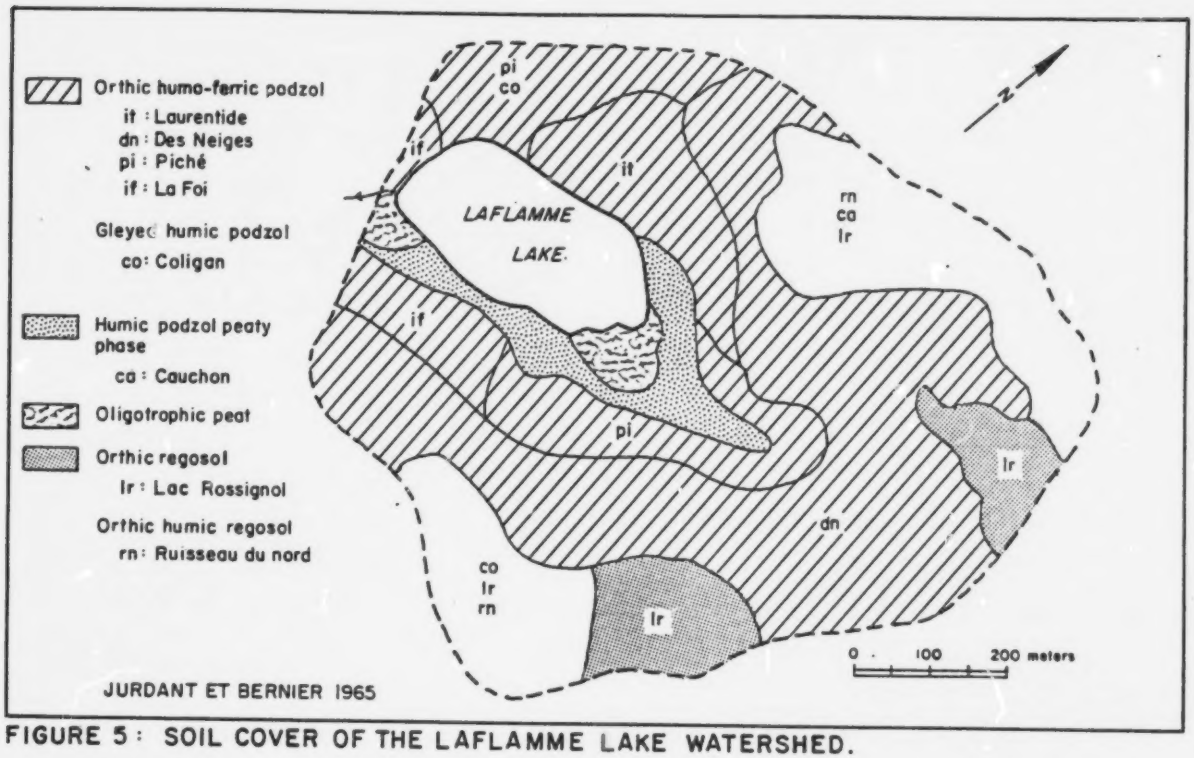

FIGURE 5 : SOIL COVER OF THE LAFLAMME LAKE WATERSHED.

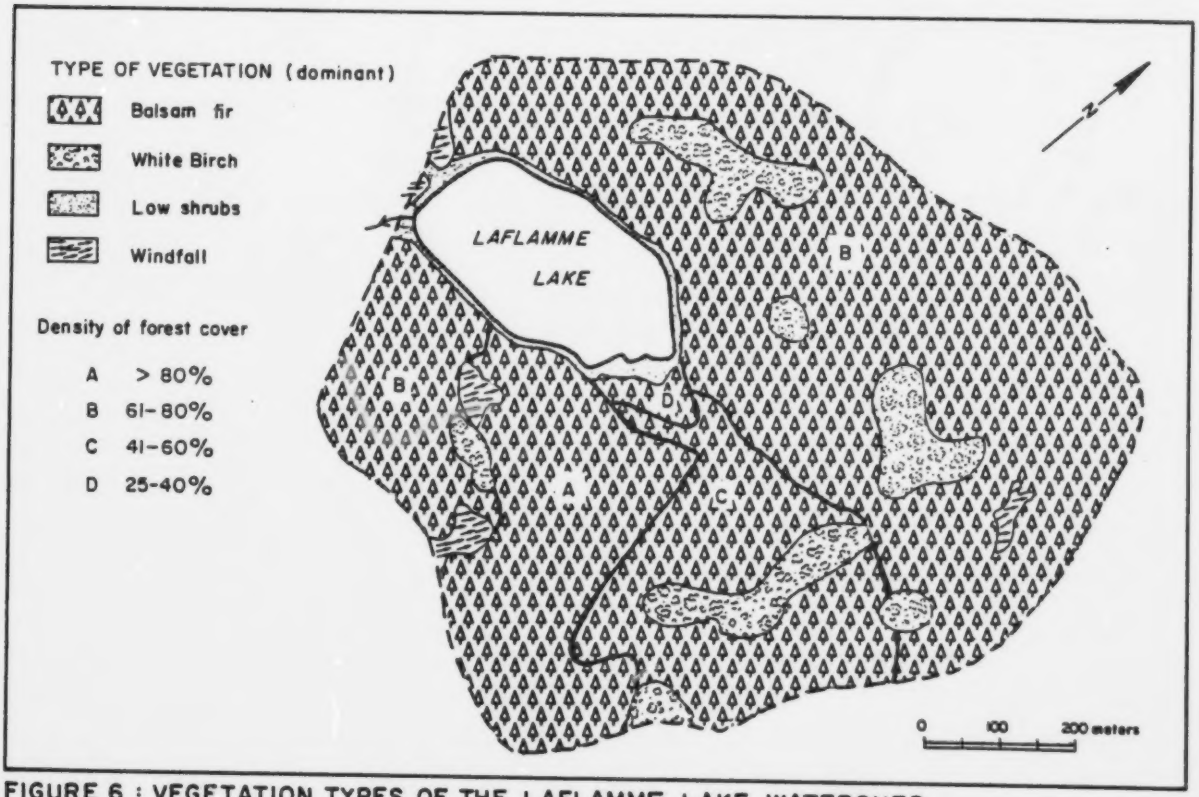

FIGURE 6 : VEGETATION TYPES OF THE LAFLAMME LAKE WATERSHED.

characterized by a compaction of the C horizon into a fragipan. The humus layer of the MOR type has an average thickness of 7,9 cm (Martel, 1981). The soil has a coarse texture and is classified as sandy loam (0-30 cm) silty sand (30-90 cm) and sand (90-120 cm) (Plamondon et al., 1983). Soil water is acidic with pH ranging from 3,3 in the H horizon to 4,7 in the lower C horizon (Robitaille et al., 1983b).

1.5 Vegetation

The watershed is covered by a boreal coniferous forest of the balsam fir-white birch climax zone. Dominant species include 90% balsam fir (Abies balsamea, Mill) 5% white birch (Betula papyrifera, Marsh) and 5% white spruce (Picea glauca, Moench) (figure 6). The forest was logged in 1943. A small area of the watershed was cleared after 1980 following dye back due to the spruce budworm epidemic (Choristoneura fumiferana, Clem). The epidemic started in the early 1970's and was less severe in 1979 and 1980 but seemed to have gained strength in 1981 and 1982. In 1982, defoliation at the main forest hydrology station on the northern slope of the watershed was estimated to be 40 to 50% (Prévost, 1983).

The average age of stems is 50 years, the density of commercial stems is 4800 stems per ha and the percent covering is 80% (Prévost, 1983). Shrubs species include: Acer spicatum, Alnus rugosa, Myrica gale, Salix sp, Kalmia polyfolia, Casandra calyculata.

1.6 Drainage Network

The drainage network within the basin is not very extensive. Inlet streams are intermittent except for the main tributary. The outlet stream is characterized by a permanent flow ranging from 0,002 m^3/s during low flow in the winter to 0,01 m^3/s in May. The stream bed is largely shaded during summer. The substrate is sand, gravel and cobbles.

Groundwater contribution to the lake recharge dominates most of the year, while surface runoff gains importance during the spring period. Drainage is good in areas far from the lake but is poor on the southshore and

in swamps (figure 7). Residence time of groundwater in the recharge area close to bedrock is less that 500 days while groundwater in the discharge area has much longer residence times (Bernier et al., 1983).

The lake itself is oval shaped with a perimeter of 1,02 km and a maximum depth of 5,3 m (figure 8). The lake volume is 125 x 10^3 m^3 and the renewal rate is about two months. Aquatic macrophytes such as Nuphar, Eleocharis, Carex, Saggitaria occupy a large area of the lake.

1.7 Water Quality

Laflamme Lake is a small low mineralized lake. The water has a distinct yellow tint with colour readings of about 23 units. Dissolved organic carbon levels are around 3,6 mg/l. The composition of lake water is dominated by calcium (0,12 meq/l), bicarbonate ions (0,11 meq/l) and sulfate ions (0,085 meq/l) The lake is considered to be highly sensitive to acidification, affected by atmospheric deposition, yet only slightly acidified (Papineau, 1983). The average pH is 6,4 although, during spring melt, values as low as 4,3 have been measured near the lake shores.

The lake undergoes two turnover periods, one in the fall and one right after ice break up in late May. When compared to other lakes in the Laurentide Reserve of which the Montmorency Forest is a part, Laflamme Lake can be considered to be somewhat less acidic than nearby lakes but having a comparable degree of mineralization. These differences are probably related to the depth and permeability of soil and surficial deposits.

1.8 Fish Population

The lake sustains a population of about 2 000 brook trouts (Salvelinus fontinalis) (Verreault et Langlois, 1984). These fish grow slowly due to low water temperatures. An average two year old may be 20 cm long. The fish spawn from mid-September to mid-October in the lake itself within 20 m of the shore. In 1981, a severe loss of fish occurred in early June and has been attributed to the simultaneous stresses of low oxygen, low pH and high aluminum levels in the lake.

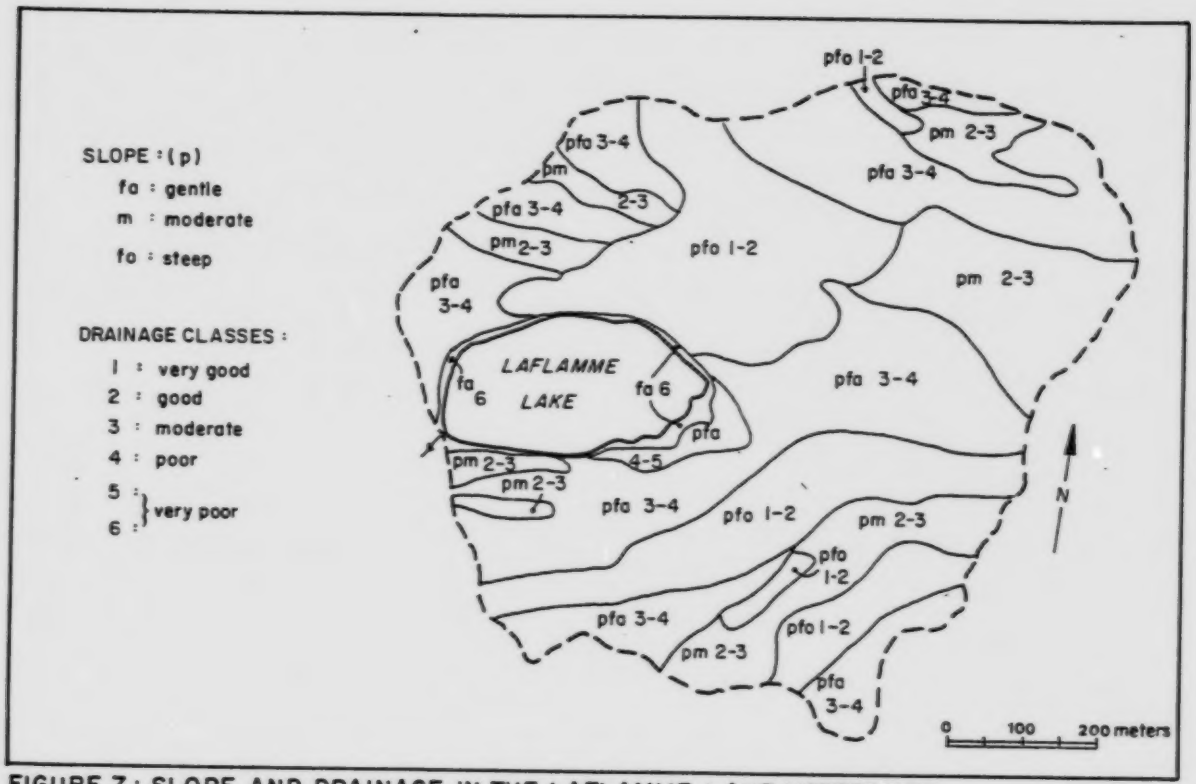

FIGURE 7 : SLOPE AND DRAINAGE IN THE LAFLAMME LAKE WATERSHED

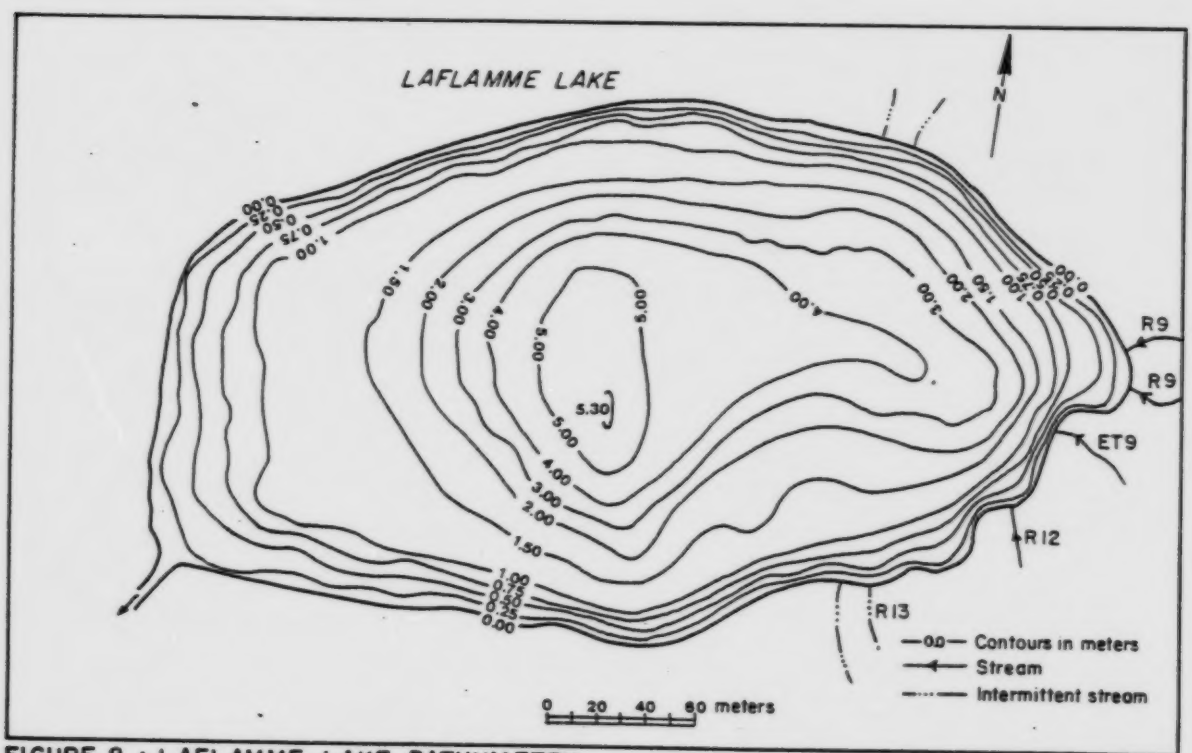

FIGURE 8 : LAFLAMME LAKE BATHYMETRY

2. METHODS

The sampling program for the main components of the ion budget study began routinely in early 1981 (table 2). Precipitation sampling is the responsibility of the Atmospheric Environmental Service (AES) of Environment Canada. The Inland Waters and Lands Branch monitors quality and water levels of the lake and of the outlet. Several other agencies and university contractants have also carried out sampling work in the watershed related to the LRTAP program. When their results are cited in this report, details of analytical methods can be found in corresponding references.

Table 2. Sampling program and published data for ion budget study.

Parameter	Initial Sampling	Last Year of Available Data	References
Lake level	Dec. 6, 1979	1985	Canada, 1982 to 1986
Streamflow	Nov. 6, 1980	1985	Canada, 1982 to 1986
Precipitation	Dec. 4, 1980	1984	Barrie et al. 1982, 1984 Wiebe et al. 1985 Vet et al. 1986
Lake water quality	Jan. 8, 1981	1985	NAQUADAT
Outlet water quality	Mar. 16, 1985	1985	Papineau, 1983, 1984, 1985

2.1 Precipitation

Both air and precipitation chemistry measurements were made on a daily basis at the Montmorency Forest station of the federal APN network (Air and Precipitation Network) established at the end of 1980. As of July 1983, the station became part of the CAPMoN (Canadian Air and Precipitation Monitoring Network) and will be refered to hereafter by the later name.

Precipitation was collected in a Sangamo wet-only sampler in a black bucket. Precipitation amount was measured by using standard Canadian meteorological service rain and snow gauges. Samples were bottled individually, stored at 4° C without preservatives and shipped in a cooled container every two weeks to the Water Quality National Laboratory in Burlington, Ontario. Precipitation samples were analyzed for pH, sulphate, nitrate, chloride and ammonium ions as well as calcium, magnesium, sodium and potassium. Total phosphorus was measured in 1981 and 1982. Methods used are described in table 3.

Ambient SO_4, SO_2 and total NO_3 concentrations were measured at a height of 10 m by drawing approximately 30 m^3 of air over a 24 hour period through filters and then extracting the filters in deionized water and analyzing.

2.2 Lake and Outlet

Weekly samples were taken at the center of the lake (integrated sample over 4 m) and at the outlet, stored at 4°C and shipped the same day to the regional laboratory in Longueuil. Samples were preserved with sulfuric acid in the case of phosphorus samples and with nitric acid for heavy metal analysis (table 4). In 1983, heavy metal analysis was transferred to the Water Quality National Laboratory and samples were shipped every three months. In the field, pH, conductivity, dissolved oxygen and temperature were measured with a Hydrolab probe at five depths (0,5, 1, 2, 3, 4 m from the surface).

Samples were analyzed for major cations (Ca, Mg, Na, K), major anions (SO_4, Cl, NO_3), conductivity, pH, alkalinity (total and Gran), colour, total phosphorus and eight heavy metals (Al, Mn, Fe, Pb, Ni, Cu, Zn, Cd). Every two months since 1985, samples from the center of the lake are also analyzed for silica, ammonium ion, dissolved organic and inorganic carbon and ion chromatographic sulphates. During the first two years of sampling, inorganic phosphorus and mercury were also analyzed but sampling was abandoned because of analytical problems. Details on analytical methods used can be obtained by consulting NAQUADAT (National Water Quality Data Bank) reference book. NAQUADAT codes are given in table 3.

Table 3. Analytical methods used for precipitation and surface water chemistry analysis

PARAMETER	PRECIPITATION METHOD		SURFACE WATER METHOD	NAQUADAT CODE
pH	Electrometric		Electrometric	10301L
Ca	Atomic Absorption		Atomic Absorption	20103L
Mg	Atomic Absorption		Atomic Absorption	12102L
Na	Flame photometry		Atomic Absorption	11105L
K	Flame photometry		Atomic Absorption	19102L
NH_4	Colorimetric		Colorimetric	7555P
SO_4	Colorimetric (MTB)	APN	Colorimetric (MTB)	16306L
	Ion chromatography	CAPMoN	Ion chrom.	16309L
Cl	Colorimetric	APN	Colorimetric	17203L
	Ion chrom.	CAPMoN		
NO_3	Colorimetric	APN	Colorimetric	7112L
	Ion chrom.	CAPMoN		
Total Phosphorus	Autoclave+digestion	APN	Digest + color.	15406P
Inorg. Phosphorus			Colorimetric	15301P
Conductivity			Electrometric	2041L
Colour			Colorimetric	2011L
Alkalinity total			Titration H_2SO_4	10101L
Alkalinity Gran			Titration HCl	10110L
Hardness			Titration	10603L
SiO_2			Colorimetric	14102L
DOC			Infrared	06104L
DIC			Infrared	06180L
Heavy metals			Atomic Absorption	
Al				13003P
Cd				48002P
Cu				29005P
Fe				26005P
Mn				25005P
Ni				28002P
Zn				30005P
Pb				82002P

APN : Methods from Barrie et al. (1980).
CAPMoN : Methods from Vet et al. (1986).

Lake level and streamflow at the outlet are measured continuously with limnigraphs. The V-notch weir at the outlet is heated during winter months to prevent freezing.

Data is validated by using ion balance calculations in which cations refer to Ca, Mg, Na, K and H and anions refer to HCO_3, SO_4, Cl and NO_3 in µeq/l:

$$25\% > \frac{\sum \text{cations} - \sum \text{anions}}{(\sum \text{cations} + \sum \text{anions})/2} \times 100$$

Calculated conductivity and outlier testing are also used for validation. Values presented in this report have not been corrected for sea-salt. Data has been stored in NAQUADAT bank in Ottawa under the station numbers 00QU02PD0001 and 01QU02PD0001.

Table 4. Sample containers and preservation for constituents in water.

Analysis	Type of Bottle	Conservation
pH, Cond, major cations major anions, alk, silica	Polyethylene 1 liter	4°C
Phosphorus	Glass 125 ml	4°C 1,25 ml H_2SO_4
Heavy metals Al,Mn,Fe,Ni,Cu,Zn,Cd,Pb	Polyethylene 500 ml	2 ml HNO_3
Ammonium ion	Glass 125 ml	4°C 0,16 ml H_2SO_4
Organic and inorganic carbon	Glass 1 liter	4°C

3. ATMOSPHERIC INPUT

3.1 Precipitation Amount

One of the main characteristics of LLW is the large amount of precipitation received during the year. Annually, there are close to 200 days with some form of precipitation.

Annual precipitation during the five hydrological years (1 June to 31 May) ranged from 1,12 m in 1981-1982 to 1,56 m in 1982-83 (figure 9). The average was 1,31 m. More than 6,5 m of water have fallen on the watershed between June 1981 and May 1986. Annual snowfall was on average about 0,43 m of water which represents 33% of incoming precipitation. The snowpack reaches heights of 1,2 m before spring thaw. The largest snowpack was measured during the winter of 1984.

Monthly distribution of precipitation is less variable over a year than that of outflow (figure 10). An average of 11 cm of precipitation falls per month. Important rain events occurred in February 1981 (11 cm), in the fall of 1982 when 35 cm of rain and snow fell in November and December, in the springs of 1983 (33 cm in April and May) and 1986. The highest recorded monthly precipitation was of 23,5 cm in May 1983. Relatively dry periods of less than 5 cm of water per month occurred in January 1981, 1984, 1985, in the late fall of 1981, in February and May 1982, in October 1984 and in August 1985. The lowest precipitation was of 2,0 cm in February 1986. Extremely wet or dry periods are important to consider as they can bring about changes in storage and water chemistry in the watershed.

On a daily basis, the amount of precipitation received by the watershed ranges from 0,1 mm to 93 mm. In 1984, heavy precipitation events (>10mm) accounted for 70% of total incoming water while events of less than 2,5 mm accounted for only 7% (Desautels, 1985). Prévost (1983) reports that the intensity of events remains below 2,5 mm. h^{-1} and 5,0 $mm.h^{-1}$ respectively during 83 and 95% of the time.

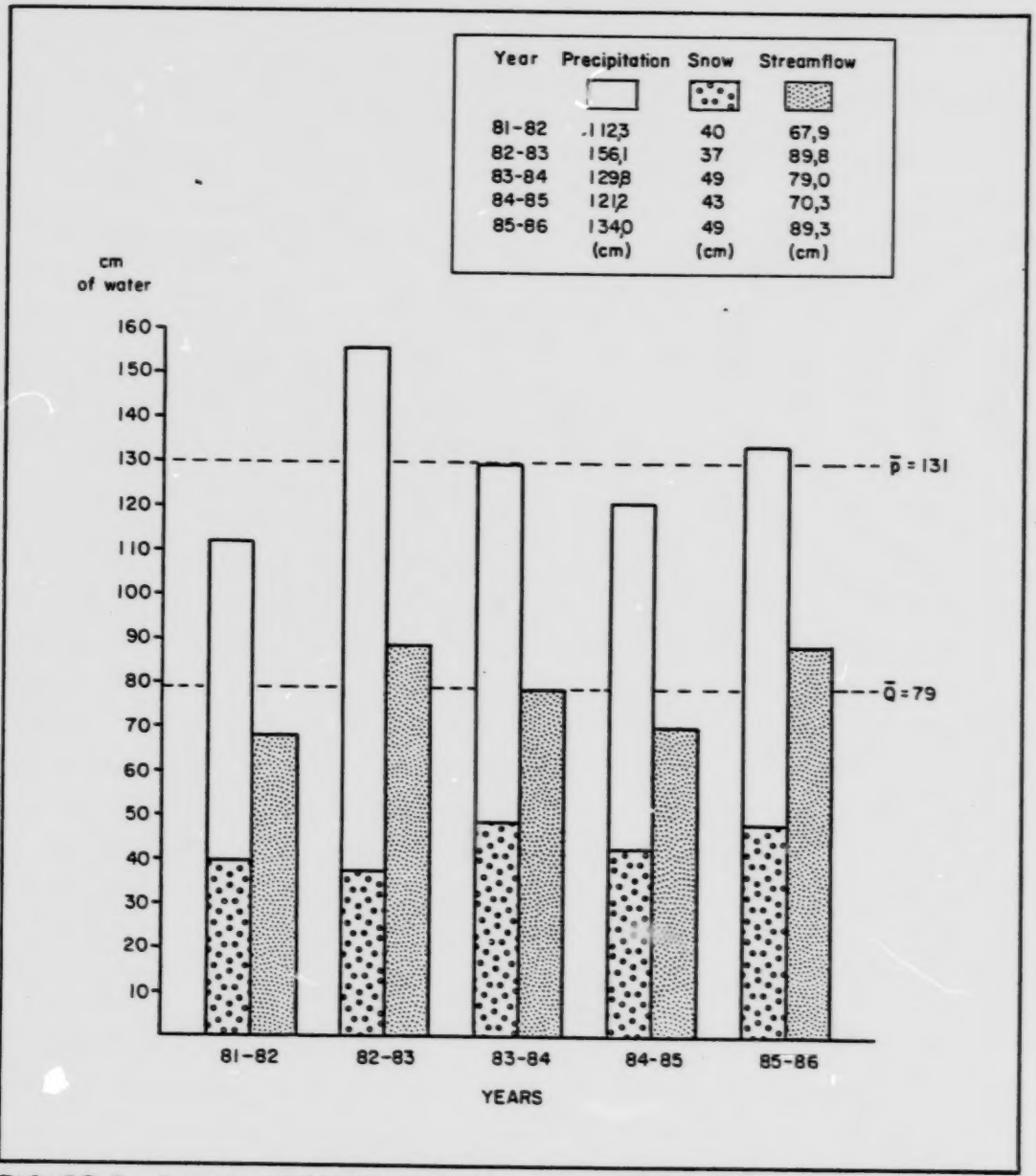

FIGURE 9 : ANNUAL PRECIPITATION AND STREAMFLOW FOR THE LAFLAMME LAKE WATERSHED.

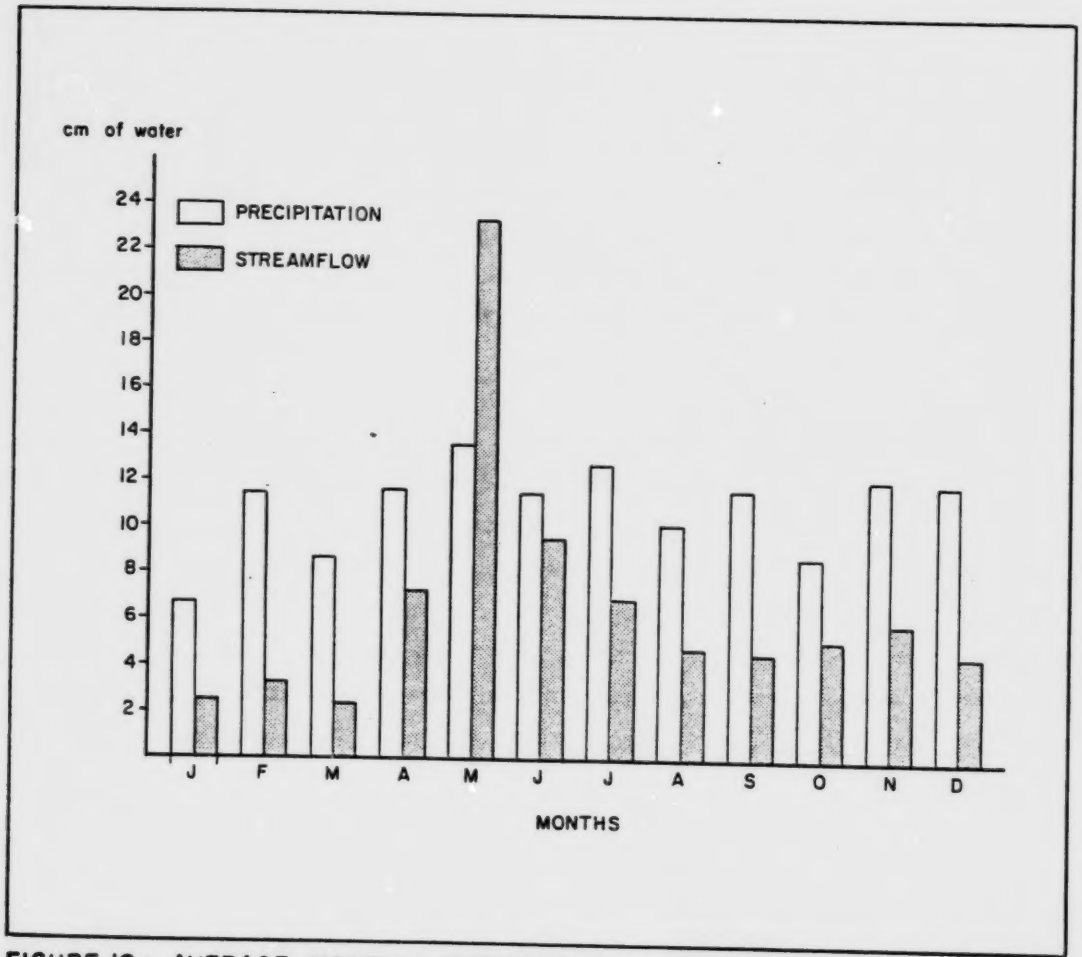

FIGURE 10 : AVERAGE MONTHLY PRECIPITATION AND STREAMFLOW FOR THE LAFLAMME LAKE WATERSHED DURING 1981 - 1985.

3.2 Ion Concentration

The quality of rain and snow can vary considerably from one event to the next as shown in figure 11 for three days in 1982. Factors that can contribute to concentration changes include type, intensity, quantity and duration of precipitation as well as antecedent conditions, air quality, meteorological parameters and origin of air masses.

Air quality and precipitation chemistry for the CAPMoN station have been published in Barrie et al. (1982, 1984), Wiebe et al. (1985) and Vet et al. (1986) as well as in the acid rain bulletins produced by AES.

3.2.1 pH

The pH of precipitation over the watershed ranged from 3,4 to 6,8 during the 1981 to 1985 period. The volume weighted average was 4,4. For more than 70% of events, the pH fell within a range of 4,0 to 5,0. About 7% of events had a pH below 4,0 (figure 12). It is considered that an event with a pH below 4,2 is very acidic while moderately acidic events range between 4,2 and 4,6.

Desautels (1985) studied weekly acid rain report data from December 1983 to December 1984 and found a relation between the acidity of precipitation and the amount, the season and the region of origin of air masses. The average acidity was found to be greater for events with smaller precipitation quantity (0,1 to 2,4 mm). The winter season was the least acidic. The precipitation from weather systems that track over heavily populated areas of the Midwestern United States are the most acidic ones and are also responsible for a large amount of the total precipitation over the watershed (table 5).

Although average acidity decreases with volume, there are however a considerable number of events in a year which contribute both to acid loading and precipitation amount. For instance, the episodic nature of deposition can be seen with 1985 data when 10 major events had an average pH of 4,0 and deposited 0,17 kg/ha of H^+ or roughly 40% of annual loading and 22 cm of water (17%) on the watershed.

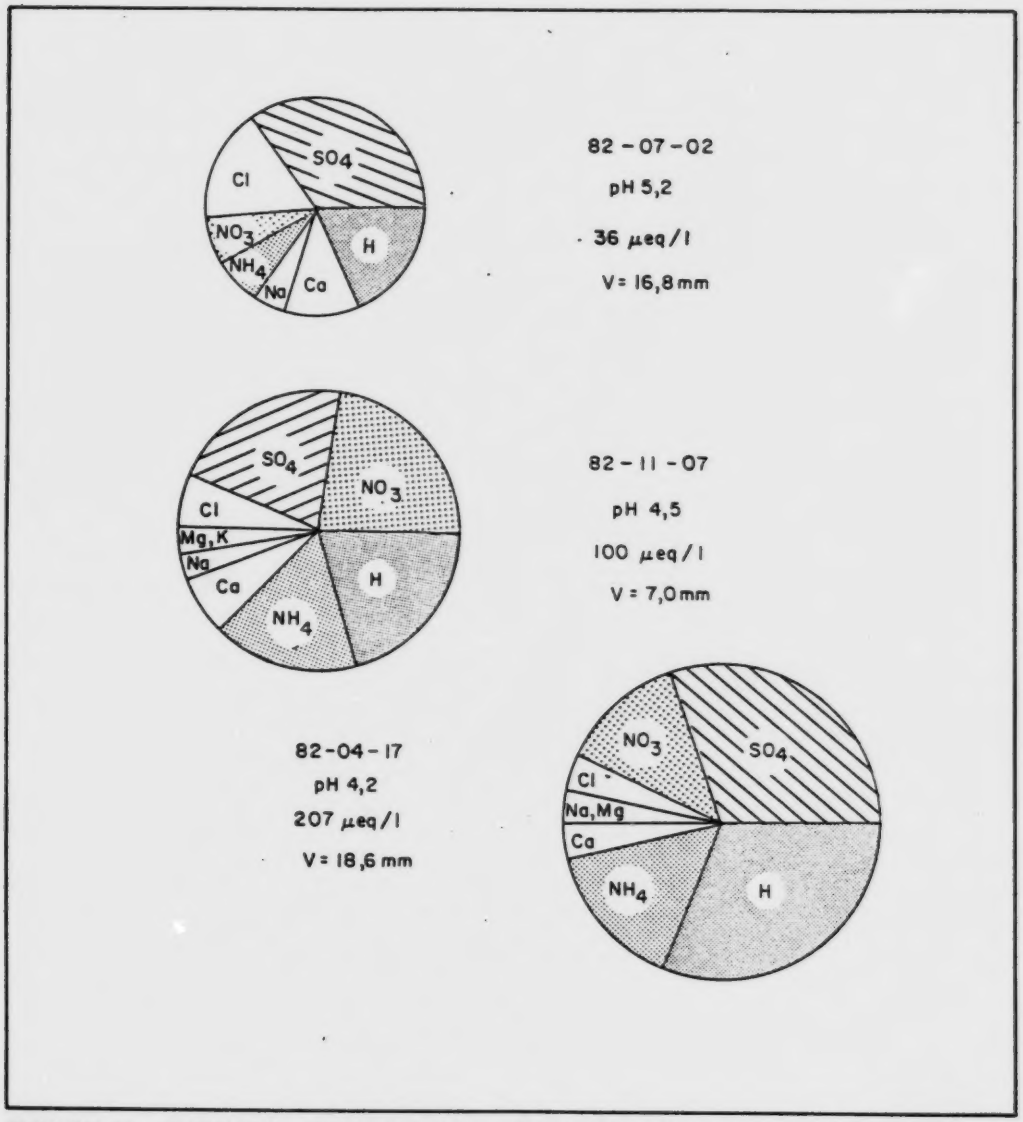

FIGURE 11 : CHEMICAL COMPOSITION OF THREE PRECIPITATION EVENTS.

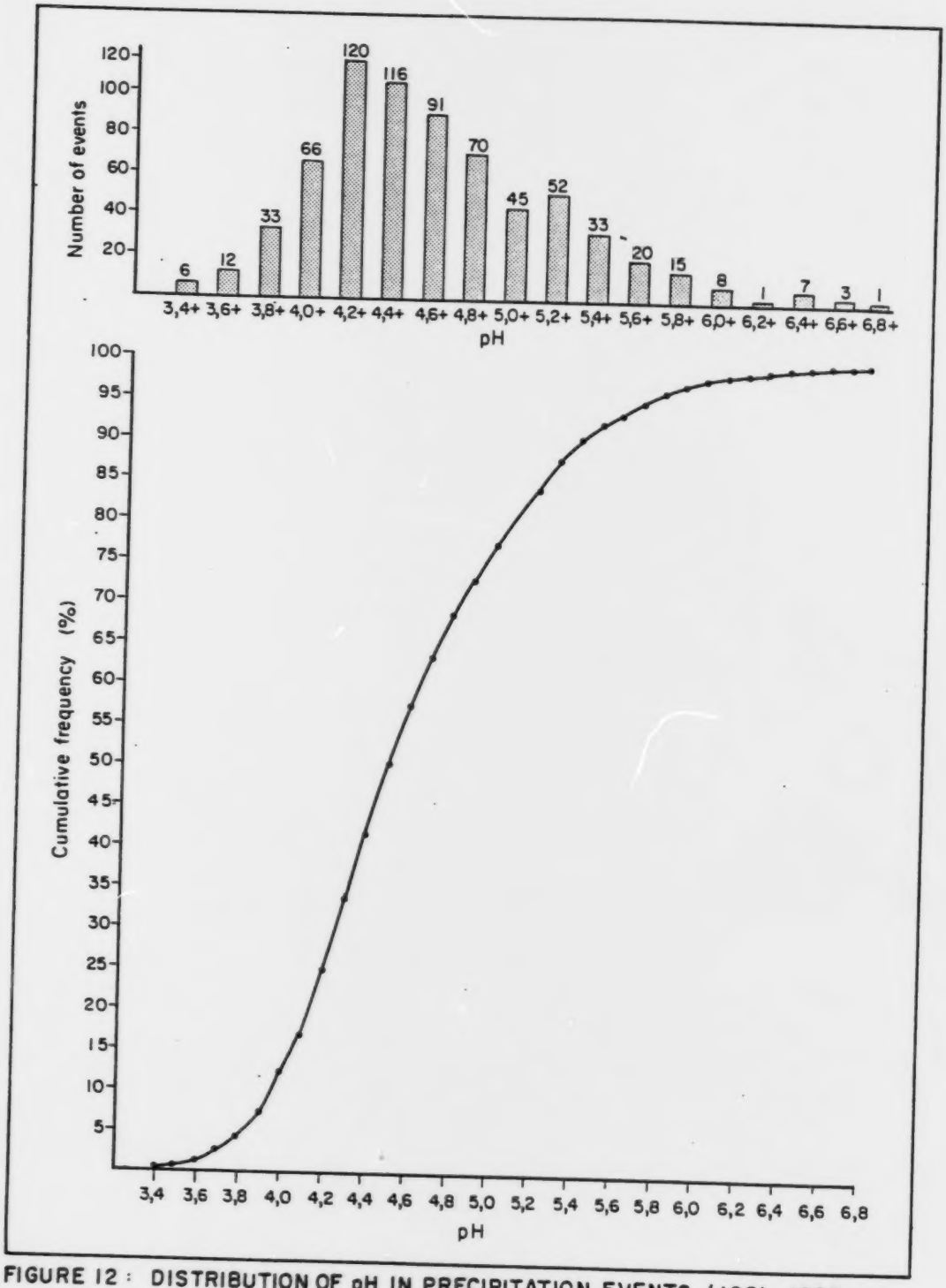

FIGURE 12 : DISTRIBUTION OF pH IN PRECIPITATION EVENTS (1981 - 1985 p)

Table 5. pH of precipitation events according to the origin of air masses. December 1983 to November 1984 (Desautels, 1985).

Origin of Air Masses	Number of Events	Amount of Water (mm)	pH
Middle West	38	253	4,05
Southern Ontario	15	107	4,29
Nothern Ontario	13	91	4,69
Nothern Quebec	18	84	4,95
Maritimes	10	112	5,08
New-England and Atlantic	12	169	4,58
Eastern coast	10	152	4,52

3.2.2 Other Major Ions

Along with the hydrogen ion, several other components are found in wet precipitation including SO_4^{--} (1,67 mg/l), NO_3^- (0,24 mgN/l), NH_4^+ (0,16 mgN/l), calcium, sodium, chloride and small amounts of magnesium and potassium. Average annual weighted concentrations are given in table 6. Total phosphorus was also measured in the first two years of operation. Close to 70% of values where in the range 0,001 to 0,005 mg/l.

Basically, precipitation falling over the watershed is a dilute solution of approximately 100 µeq/l of sulfuric and nitric acid. Concentrations of sulphate and nitrate ions differ from year to year with highest values measured in 1984. On an equivalent basis, usually, sulphate and hydrogen ions are the major components but during winter months, especially January, nitrate values can equal or exceed those of sulphate ions. Summers and Barrie (1986) report a strong seasonal variation in the SO_4^{--}/NO_3^- ratio for the region extending from the states south of the Great Lakes across New England and south eastern Canada. Chemical oxidation rates of SO_2 and NO_x in the atmosphere seem to be a major controlling factor of S/N in precipitation rather than variations in emissions.

There exists a seasonal cycle in precipitation quality (figure 13). In the warm season, high values of sulphate, hydrogen and to some extent ammonium ions are measured. These three parameters also follow similar patterns of variation during the rest of the year. Nitrate values tend to be higher in the winter than in summer but differences are smaller than those of sulphate or hydrogen ions. Taken together, sulphate and nitrate make up 92% of the total anionic strength of precipitation.

Monthly concentrations of all parameters are listed in annex 1. Some analytical problems did occur with sodium, chloride and calcium determinations and values were omitted when necessary.

Table 6. Weighted annual concentrations of dissolved substances in precipitation for the Laflamme Lake Watershed.

Substance	1981			1982			1983			1984			Mean	
	mg/l	µeq/l	%	mg/l	µeq/l	%	mg/l	µeq/l	%	mg/l	µeq/l	%	mg/l	µeq/l
H^+	0,03	27,6	59	0,04	41,5	69	0,03	31,1	59	0,04	44,2	63	0,04	36,1
NH_4^+	0,13	9,3	20	0,15	10,5	17	0,16	11,4	22	0,20	13,9	20	0,16	11,3
Ca^{++}	0,09	4,6	10	0,07	3,7	6	0,11	5,6	11	0,16	8,1	11	0,11	5,5
Na^+	0,08	3,7	8	0,08	3,5	6	(0,06	2,8	5	0,03	1,3	2)	0,06	2,8
Mg^{++}	0,01	1,2	2	0,01	0,8	1	0,02	1,3	2	0,02	1,9	3	0,02	1,3
K^+	0,02	0,5	1	0,02	0,5	1	0,02	0,6	1	0,03	0,7	1	0,02	0,6
SO_4^{--}	1,44	30,0	64	1,77	36,9	61	1,40	29,0	61	2,06	42,9	59	1,67	34,7
NO_3^-	0,20	14,5	31	0,26	18,9	31	0,19	13,5	29	0,30	21,7	30	0,24	17,2
Cl^-	0,08	2,1	5	0,17	4,7	8	0,16	4,6	10	(0,29	8,1	11)	0,17	4,7
pH	4,56			4,38			4,51			4,36			4,44	
Cations		46,6			60,5			47,1			72,7			
Anions		46,9			60,5			52,8			70,1			

( ) : Volume analyzed is less than 50% of total volume.

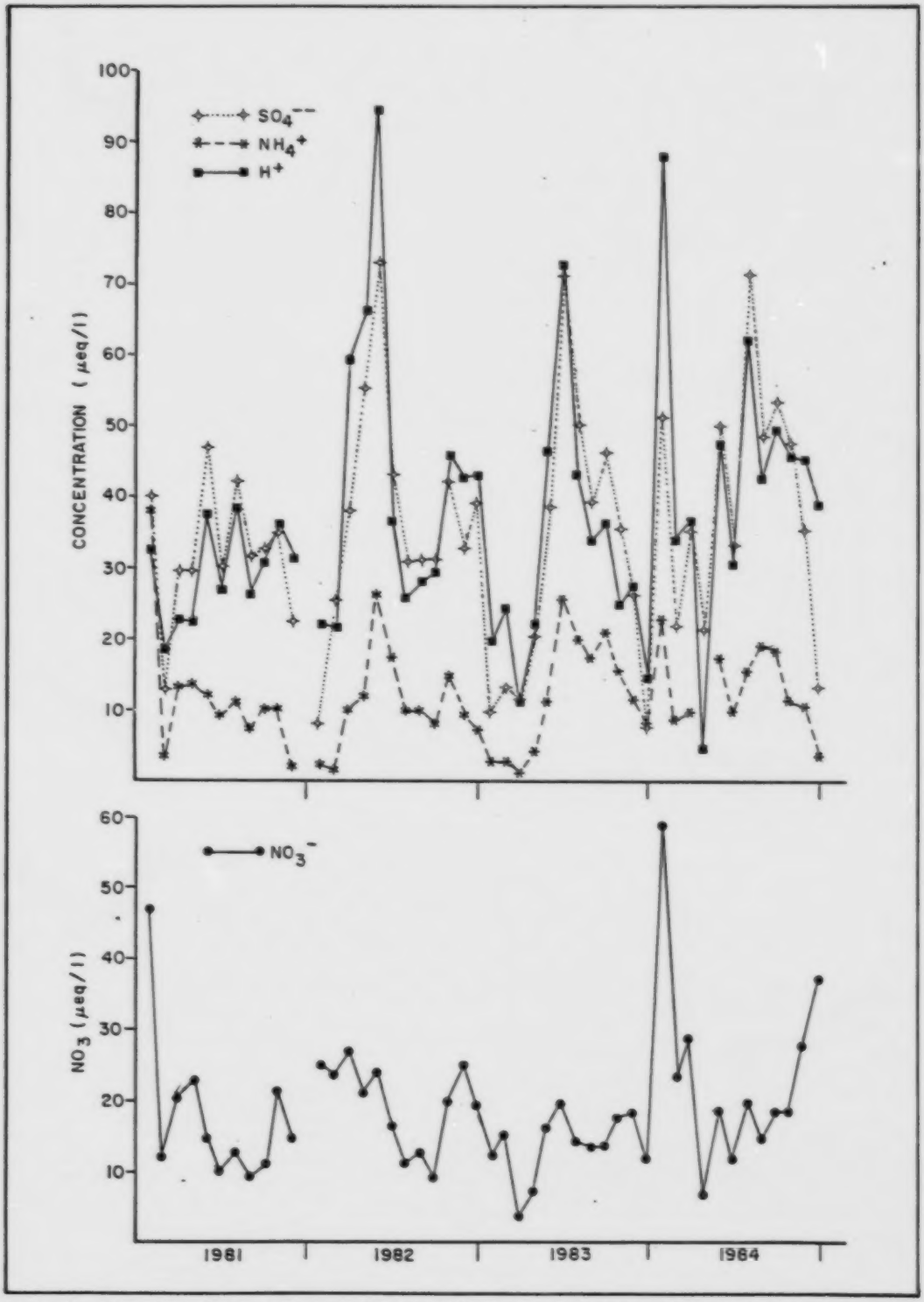

FIGURE 13 : MONTHLY WEIGHTED CONCENTRATIONS OF MAJOR IONS IN PRECIPITATIONS OVER LAFLAMME LAKE WATERSHED.

Correlation analysis was carried out and r^2 values of 0,67 and 0,31 were obtained for $H\text{-}SO_4$ and $H\text{-}NO_3$ pairs respectively. Multiple regression using both sulphate and nitrate leads to:

$$pH = 4,97 - 0,21\ [\ SO_4^{--}] - 0,54\ [\ N\text{-}NO_3^{-}]\quad r^2 = 0,79$$
$$N = 48$$
$$[\ ]\ \text{in mg/l}$$

In a regression carried out against time, there was a slight positive but not statistically significant slope for all three parameters.

Relative composition of precipitation is quite similar to that available for the Adirondack Mountains for the period of November 1978 to October 1984 (Raynal, 1985). In the Adirondacks, the composition is as follows: sulphate (62,7%), nitrate (32,4%), chloride (4%) hydrogen ion (61,9%), ammonium ion (18,6%) calcium (8,9%), sodium (6,5%)). The average pH is however lower being 4,15. When comparing patterns in monthly concentrations, those of sulphates are more similar than those of nitrate, which is probably caused by the fact that nitrates are usually associated to a greater degree with local sources such as automobiles rather than distant sources.

Data is also available since 1983 from the Quebec provincial network. Grimard (1985) reports that the annual pH over the province ranged from 4,2 in the southwestern region near the Ontario border to 5,0 in the north above the 50th Parallel. Sulphate and nitrate concentrations followed à similar spatial gradient and ranged from 0,6 to 3,0 mg SO_4/l and from 0,09 to 0,56 mg N/l. Wet deposition of sulphate ions ranged from 5 kg/ha in Schefferville to 32 kg/ha northwest of the Ottawa-Hull region. Nitrate deposition was highest near Montreal (9,0 kgN/ha).

3.3. DEPOSITION

It is not only the concentration of ions in precipitation that is important in determining an effect on an ecosystem but also the deposition which is the total amount of a given substance that is received. Deposition

takes place via three processes: removal by rain and snow (wet deposition), direct uptake of particules and gases at the earth's surface (dry deposition) and fogwater deposition, the least studied of the three.

3.3.1 Wet Deposition

Wet deposition can be obtained by summing the product of the invididual sample concentration of a given species by the amount of precipitation. Annual results for LLW are given in table 7.

Deposition of sulphate is close to 20 kg/ha while nitrate deposition averages 3,3 kgN/ha. Hydrogen ion deposition is close to 0,5 kg/ha or 48 mmole/m^2. Wet atmospheric deposition will be discussed in further detail in the mass balance section of this report.

3.3.2 Dry deposition

Unlike wet deposition, dry deposition is not measured directly but is obtained by the product of daily mean air concentration, the dry deposition velocity coefficient and the average time. Average concentrations of SO_2 and particulate sulphate at the Montmorency Forest site are 1,05 µgS/m^3 and 0,59 µgS/m^3 respectively. A study of dry deposition has been carried out for Eastern Canada by Barrie and Sirois (1986). They found that although the total annual deposition over the area is of 10 to 86 mmole/m^2 sulphate (9,6 to 83 kg/ha) and 13 to 62 mmole/m^2 nitrate (1,8 to 8,7 kgN/ha), only an average of 22% of total sulphate deposition and 30% of total nitrate deposition is dry deposited. Of the six locations studied, the contribution of dry deposition to total sulfur deposited was lowest at Montmorency Forest (14%). At the same site, dry deposition of nitrate without NO_2 dry deposition being considered was 17% of total deposition (table 8). This fraction would increase if NO_2 deposition were included.

These results are rather low compared to results in Europe where Rodhe and Granat (1983) estimated the fraction of annual dry deposition at 50%. However studies in the United States (Lovett & Lindberg, 1984; Arland et al., 1985; Raynal, 1985; Dasch, 1986) come up with results closer to those

Table 7. Annual atmospheric wet deposition for Laflamme Lake Watershed.

Substance kg/ha	1981	1982	1983	1984	mean	1981-82	1982-83	1983-84
SO_4^{--}	19,39	21,14	23,96	23,23	21,9	18,28	22,61	23,30
H^+	0,38	0,50	0,52	0,51	0,48	0,43	0,52	0,47
$N\text{-}NO_3^-$	2,91	3,36	3,17	3,66	3,28	2,73	3,27	3,32
$N\text{-}NH_4^+$	1,77	1,74	2,6e	2,27	2,1	1,38	1,83	2,98
Cl^-	1,12	2,11	---	---	1,6	1,52	1,85	---
Ca^{++}	1,25	0,93	1,91	2,0e	1,5	0,96	0,95	2,43
Na^+	1,22	1,07	2,0e	---	1,1	0,94	0,88	---
K^+	0,27	0,22	0,39	0,30	0,3	0,20	0,30	0,38
Mg^{++}	0,19	0,13	0,26	0,27	0,2	0,13	0,15	0,34
cm of Water	136,9	123,7	167,2	116,5		115,7	160,9	133,8

e: estimated

of Barrie and Sirois (1986). Raynal (1985) estimated the fraction of dry deposition in total deposition to be between 13 and 18% for sulphate and between 11 and 19% for nitrate in the Huntington Wildlife Forest, New York. Arland *et al.* (1985) report dry deposition to be 12% of total sulphate deposition and 10% of total nitrate deposition.

Table 8. Contribution of dry deposition to total deposition at the Montmorency Forest site.

Year	Total SO_4	Dry	Total NO_3	Dry
	kg/ha	%	kgN/ha	%
1981	24	16	3,6	26
1982	26	12	3,9	28

4. PATHWAYS OF WATER AND CHEMICALS TO THE LAKE

The lake watershed system can be divided into a network of compartments: atmosphere, canopy, snowpack, vegetation, soil horizons, stream segments and lake. Each compartment can affect waterflow and water chemistry through various biological, chemical or geological processes. Some processes can be quantified, others remain harder to evaluate.

4.1 Incoming Precipitation

The amount of precipitation over an area is known to vary with various physical factors such as altitude, type, age, density of cover. Plamondon (1982) measured incoming rain at five sites in the watershed for two summers to see if any important local variability occurred within the watershed or with the nearby CAPMoN station. The amount of rain varied little from one site to another. He also established a relation with precipitation amount available at the CAPMoN station (P = 0,97 Pcapmon). Because precipitation quality is considered to have less spatial variability than amount of precipitation, it is assumed that the quality of incoming precipitation over the watershed is equivalent to that at the CAPMoN station.

4.2 The Influence of Vegetation

Forests are not simply passive recipients of incident precipitation. They affect both the amount and the ionic deposition received by the forest floor. Water coming into contact with the canopy can be intercepted and evaporated. Chemical changes are also caused by washoff and dissolution of particles and aerosols deposited on vegetation (dry deposition), chemical reaction in liquid phase, leaching from the foliage and chemical uptake by vegetation. Chemically altered precipitation is termed throughfall if it falls from leaves and branches of trees or stemflow if it runs down the trunk.

The decrease of the amount of water in the forest canopy was studied during the summers of 1981 and 1982. Plamondon and Prévost (1982) evaluated

that interception by the canopy amounted to 32% of incident rainfall (table 9). Throughfall represented 66% of incident rain while stemflow was low at 1 to 3%.

Table 9. Canopy water budgets for the summers of 1981 and 1982.

Period	Pi cm	Pt cm	Ps cm	Pnet cm	I cm
June-Sept. 1981	61,6	40,2	1,6	41,8	19,8
% Pi	100	66	2,6	68	32
June-Sept. 1982	50,5	33,1	0,6	33,7	16,9
% Pi	100	66	1	67	33

P: precipitation I: interception i: incident t: throughfall s: stemflow

In the case of precipitation quality, as a rule throughfall usually shows an enrichment in most base cations, except the ammonium ion, and in acid anions. Deciduous trees generally increase the pH of incident precipitation during summer months while coniferous trees decrease the pH of incident precipitation (Arland et al., 1985). As LLW is covered almost entirely by coniferous species, very little neutralization capacity would be expected as shown by field studies (table 10).

Robitaille et al. (1983b) found that only nitrate and ammonium ion concentrations decreased in throughfall probably due to biological assimilation. There were increases in potassium, calcium and magnesium due to foliar exudation from needles of elements recycled from the soil. The increased acidity of rain at the forest floor was attributed to increases in organic acids from the vegetation. Increases in sulphates, sodium and chloride were caused by washout of dry deposition. Stemflow concentrations were higher than those of throughfall. However due to the small amount of water coming into contact with the tree trunks, the contribution to the total ionic loading to the lake is small.

Table 10. Concentration (μeq/l) of major ions in various components of the forest canopy, June to October 1982.

Ions	Incident Precipitation	Throughfall[1]	Stemflow[1]	Soil Percolate[2] Far	Near Lake
pH	4,50	4,40	4,14	4,87	5,55
H^+	31,5	39,8	72,4	13,5	2,8
Ca^{++}	3,8	24,9	113,8	122,4	129,7
Mg^{++}	0,8	10,7	37,7	28,7	62,6
Na^+	2,8	13,0	16,2	30,9	47,2
K^+	0,5	19,8	148,5	7,1	1,1
NH_4^+	12,0	trace	2,0	0,4	0,5
SO_4^{--}	35,1	73,6	198,4	111,3	47,6
NO_3^-	13,3	0,2	1,5	171,2	5,8
Cl^-	3,9	17,2	24,6	21,3	14,8
PO_4^{-3}	---	7,8	133,5	0,1	0,3

1. Robitaille (1983)
2. Robitaille et al. (1983b)

Table 11. Approximate forest canopy ion budget. June to October 1982.

Substance	Deposition Wet kg/ha	Deposition Wet+Dry kg/ha	Throughfall kg/ha	Stemflow kg/ha	Total at Forest Floor kg/ha
Gains					
SO_4	8,46	9,7	12,3	0,5	12,8
K	0,11		2,6	0,3	2,9
Cl	0,69		2,1	0,05	2,1
Ca	0,38		1,7	0,1	1,8
Na	0,32		1,0	0,02	1,0
Mg	0,05		0,4	0,02	0,5
Losses					
H	0,16		0,135	0,004	0,14
NO_3	0,93	1,0	0,009	0,001	0,01
NH_4	0,84		trace	0,006	0,01

A very rough estimate of the ionic deposition at the forest floor level for the warm months of the year is given in table 11. For the remaining months, snowpack dynamics come into play.

4.3 The Snowpack and Meltwaters

During colder months, changes in precipitation quality as it passes through the canopy may still occur but to a much smaller degree than in the summer. Interception losses are considerably reduced but evaporation can still take place during the winter. The snowpack itself also goes through many types of changes both in structure and composition.

A typical snowpack in LLW can be described as a succession of strata from previously fallen or redistributed snow in differing stages of metamorphism of snow crystals, often separated by distinct ice crusts. Its ionic content is a balance between addition due to wet and dry deposition, in-pack chemical transformations and losses in meltwater. In some cases there may also be exchanges at the interface with the soil and canopy derived litter. Several in-pack processes that have been identified are cation exchange, litter decompositon, ion migration, biological activity, rejection of impacted aeorosols by snow crystals and adsorption or desorption on particles of organic debris or minerals. The combined effect of these reactions can lead to appreciable changes over short periods of time although not during periods of very low temperatures when snowpack dynamics and in-pack rates of transport of pollutants are considerably reduced.

Snowpack quality for the winters of 1983, 1984 and 1985 are given in table 12. In 1983, higher concentrations of base cations (Ca, Mg, Na, K), chloride and sulphate ions are seen in the snowpack than in the incoming precipitation probably due to the forest canopy. Increases however are not as important as when rain passes through the canopy in summer months. The uptake of nitrate and ammonium decreases in winter as values are higher in the snowpack than in precipitation.

Table 12. The quality of incident precipitation and the snowpack during winter.

Year	1983		1984			1985
µeq/l	Pi Jan/Mar	snow[1] 15Mar/7Apr	Pi Dec/Mar	snow[2] 28 Jan	16 Mar	snow[3] 27 Mar
pH	4,7	4,7	4,5	4,4	4,6	4,6
H^+	19	22	32	43	26	28
$SO_4^{=}$	12	21	21	19	6	20
NO_3^-	11	24	23	36	21	25
Cl^-	4	9	8	3	5	3
Ca^{++}	2	5	5	< 1	2	9
Mg^{++}	0,7	2	1,2	0,2	0,3	3
Na^+	1,5	3	-	2	2	2
K^+	0,4	10	0,5	-	0,5	6
NH_4^+	2	8	10	6	1	7

1. Jones et al. (1984) 2. Jones and Bougie (1984) 3. Jones et al. (1986)

Table 13. The quality of snowpack, meltwater and runoff in 1985. (Jones et al.,1986)

Ion µeq/l	Snowpack 24 April	Meltwater 25 April-16 May	Shallow flow 25 April - 29 May
H^+	23,4	26,0	27,8
NH_4^+	8,8	7,1	0,8
Ca^{++}	5,5	10,9	75,1
Mg^{++}	2,5	2,8	18,1
K^+	5,9	5,0	11,9
Na^+	3,1	3,0	23,6
$SO_4^{=}$	13,5	19,8	103,6
NO_3^-	18,7	19,3	48,1
HCO_3^-	0,0	0,0	0,9
PO_4^{-3}	2,2	2,2	3,2
Cl^-	4,2	5,2	9,3
TOTAL	87,8	101,4	322,4

The 1983 budget for the snowpack established by Jones et al. (1984) showed additional input of all ionic species except H^+ as compared to incoming precipitation which they attribute to dry deposition, leaching of organic debris in the snowpack by rain and meltwater as well as leaching of the forest canopy by rain and wet snow.

Work by Jones and Sochanska (1985) indicates that the influence of organic debris from trees may play an important part in quality changes in the snowpack of LLW. They measured changes in snowpack chemistry especially H^+ and K^+ that they attributed to the presence within the snowpack of large quantities of organic matter fallen from the trees. Other possible roles of organic matter could be to increase orthophosphate and dissolved organic carbon concentrations and to harbour microbial activity that may lead to nitrate decreases due to absorption.

Snowpack values in 1984 illustrate the effect of melting on the concentrations of ions. The pH of the snowpack however is not greatly modified. Considerable attention has been focused on the initial period of snowmelt as ion migration becomes more important in the snowpack and high concentrations of chemicals can be found in the first meltwaters.

Jones et al. (1986) found that major ions, NO_3^- and SO_4^{--}, seem to have both differing migration rates through the pack and net losses. Nitrates seemed to be either preferentially retained or either taken up in the pack when compared to sulphates. Preferential losses of ions from the snowpack were observed during early melt events in 1983 and 1984 (Bédard, 1984; Jones et al., 1986). The first meltwaters collected in the upper strata of the 1983 snowpack were very acidic with a pH of 4,0. From April 24, 1983 to May 2, the H^+ ion losses from the snowpack occurred at a rate of 0,65 meq/m^2/d while the decreases were much lower from May 2 to May 12 being only of 0,1 meq/m^2/d.

Seip (1980) explains meltwater concentration effects by the relatively low solubility of inorganic compounds in ice. As the snowpack changes, a network of veins is formed through which meltwater passes and thus

dissolves the impurities at the snow crystal surfaces. This results in a higher concentration of acidity in the first meltwater than the average acidity of the snowpack.

Although concentrations of major ions (H^+, SO_4^{--}, NO_3^-) usually decrease in meltwater as snowmelt progresses, Bédard (1984) reports that important increases could be seen after rainfall or periods when chemicals can concentrate again due to partial freeze thaw cycles in the snowpack later on in the spring. Also concentrations may increase in meltwater if the rate of flow decreases thus allowing a longer contact time with the snowpack. Changes may also occur if additional organic matter is added to the snowpack once melting has begun or if warm weather increases biological activity.

Meltwater quality changes to a great degree over a few weeks. The main effects of meltwater on the chemistry of receiving waters are two fold. Depending on the conditions during spring melt, there may be a marked depression in pH and alkalinity and peak concentrations of NO_3 and NH_4 following the influx of concentrated acidic water from the initial melt period. On the other hand, for ions with lower concentrations in meltwater than in surface waters (base cations and sulphate), a dilution is likely to occur. However not all meltwater enters the lake directly. Water may come into contact for some amount of time with the litter layer or deeper horizons of the soil where important chemical changes can occur. Water can then enter the lake by overland flow, shallow flow, streamflow and groundwater flow.

4.4. Overland Flow and Shallow Flow

Overland flow, although not very extensive in the watershed, becomes more important in the spring. During this period, shallow flow and pipeflow also increase. These three pathways of water to the lake can be considered to be rapid types of flow with some contact with the litter and humus layer of the soil. Most of the information on shallow flow has been obtained during spring melt studies.

Jones et al. (1984) report that shallow hypodermic streams have much higher values of base cations, sulphates and nitrates than either meltwater or the snowpack (table 13). The concentration of ammonium ions however decreases, which is attributed to transformation or assimilation by biological processes. The large change in the proportion of sulphate to nitrate ions in shallow flow lead Bédard (1984) to suggest that the soil acted as a reservoir for both ions during the spring but different processes occurred for each ion. Nitrate from microbiological activity would be washed out of the surface soil layer with a higher content of organic matter while sulphate would be mobilized to a greater extent by physical desorption. Surprisingly, nitrate concentration in hypodermic flow decreased exponentially with time while both acidity (20-40 µeq/l) and sulphate values (85-116 µeq/l) remained rather constant indicating that the stream may have been influenced by deeper neutralizing groundwater.

4.5 Recharge Streamflow

The network of streams in the recharge area is not very developed. There exists one small inlet (ET9) and two or three even smaller side streams (figure 8). The water quality of these streams was also measured by Jones et al. (1984) in the spring of 1983 (table 14). As sampling began before the spring melt, the range of concentrations included both winter and spring values which gives a good idea of the range of annual values. Stream water composition was similar to that of the lake and the outlet. The quality of the streams in the recharge area seemed to be controlled by groundwater.

As in most surface waters, there was an inverse relationship between increased flow in the spring and Ca, Mg, HCO_3 and Na concentrations. The values of H^+ seemed to increase with flow and important pH depressions were seen in the spring (pH < 5,0). K and Mn levels were found to increase with increases in the acidity level. The relation between total aluminum levels and acidity was less clear. In 1983, total aluminum levels increased from 90

Table 14. Stream water quality in 1983 (Jones et al., 1984)

Parameter		Permanent Stream: (ET 9)[1] Range	Mean	Intermittent Stream: (R 12)[2] Range	Mean
pH		4,6 - 6,6	5,7	4,2 - 6,5	5,7
Cond.	µS/cm	14 - 33	20	13 - 31	20
Ca^{++}	µeq/l	44 - 189	101	51 - 185	109
Mg^{++}	µeq/l	13 - 43	25	14 - 57	32
Na^{+}	µeq/l	7 - 62	32	15 - 61	34
K^{+}	µeq/l	5 - 19	11	6 - 14	9
NH_4^{+}	µeq/l	0,3 - 10	1	0,4 - 1,5	0,3
SO_4^{--}	µeq/l	48 - 89	73	49 - 88	71
HCO_3^{-}	µeq/l	1 - 149	43	2 - 168	64
NO_3^{-}	µeq/l	18 - 43	30	13 - 44	23
Cl^{-}	µeq/l	3 - 24	8	3 - 30	10
Total anions			157		171
Total cations			177		197

1. March 15 to May 30, 1983.
2. March 29 to May 30, 1983.

to 190 µg/l from early April to the end of May despite several rapid dilutions (Jones et al., 1984). In 1985, Campbell et al. (1986) found a good relation between patterns of variations in pH, Al and DOC. Aluminum increased from 50 to 250 µg/l, pH decreased by up to 2 units and DOC levels doubled. The relative proportion of different forms of Al changed in both years. Sulphate concentrations remained much less variable than expected. Some type of mechanism may be at work which limits the amount of change that would be expected by a massive input of acidic meltwater to the system. It may be the same type of mechanism that operates during other months of the year to neutralize incoming precipitation.

4.6 Soil Characteristics and Processes.

Input ion concentration, soil contact, weathering replacement, anion retention, base cation buffering, salt effect-alkalinity depression and in-lake processes have been identified as possible controls on surface water chemistry in a watershed. Many of these controls are related to the soil. Soil processes occur within specific soil horizons and which processes are dominant depends upon which soil horizons have the longest contact with water passing through the watershed.

In LLW, the dominant type of soil, considered here to be the first meter or so below the surface, is orthic humo-ferric podzol. The soil is acidic. In fact, the acidity of water in the surface/litter zone is often greater than that of incoming precipitation. However, the pH of soil water increases with depth indicating that the soil contributes considerable H^+ buffering. Values above a pH of 4,7 have been measured in the C Horizon (Robitaille et al., 1983b). The surface layer of the soil has a high organic content (23-29%) and a greater buffering capacity than the mineral soil (Rutherford et al., 1985). The cation exchange capacity of the mineral soil is low. Soil nitrogen values begin at greater than 1% in the surface and decrease rapidly to 0,2% to 0,3% at 10 to 15 cm and eventually to about 0,15% at 40 to 50 cm. Detectable amounts of sulfur were found only in the LH horizon (0,13%). The background value in the mineral soil is 0,03%. Soils in

the watershed where also found to have a region of low Fe and Al values at about 10-15 cm just below the organic layer. Immediately below the Ae horizon occurred a darker zone where both Fe and Al values were high (Rutherford et al., 1985).

Soil water composition is given in table 10 at two LLW sites (Robitaille et al., 1983b). As seen by the water quality of shallow flow, the organic layer may be a source of many ions. The buffering of acidic inputs however occurs as water moves into the mineral soil. The rates of movement in various soil compartments were computed by Bobba et al. (1986). The half life residence times for the upper soil (0,5 m), the lower soil (0,75 m) and the groundwater zone (5,5 m) were 1,5, 8,7 and 11,2 days respectively.

As water percolates into the soil, biotic processes can transform chemical constituents such as NH_4^+, NO_3^- and SO_4^{--} altering at the same time the acid-base balance, organic content and sulfur chemistry of soil water. The fate and mobility of NO_3^- and NH_4^+ are even largely controlled by such biological processes since N is usually a limiting macronutrient and may be retained by plant uptake and microbiological processes.

Base cations (Ca, Mg, Na, K) concentrations can be altered by inputs from weathering or by base cation exchange. The difference in the two processes resides in the reversibility of the reactions, weathering not being reversible. Cation exchange is a consequence of the negative electric charges on the colloidal clay and humus particles of the soil matrix. As upper soil horizons are richer in humus it follows that exchange reactions are likely to be more important there than in lower soil layers. If the pH is greater than 4,5, H^+ exchanges with base cations if the pH is less than 4,5, H^+ will exchange with Al^{3+} (Harvey et al., 1981). Weathering releases base cations to replenish the supply. In work carried out by Rutherford et al. (1985), leaching rates (input + mineralization + cation exchange - uptake by vegetation) for LLW soils were found to be of 11 kg/ha Ca, 5 kg/ha Al, 4 kg/ha K and 3 kg/ha Mg.

Increases in aluminum can occur in soil solution at low pH but it is not always clear if the increase in Al is due to exchange reactions or to increased solubility, as aluminum solubilization is considered to be pH dependent. If aluminum is washed out of the LHF layer, it does not necessarily leave the soil since it can be precipitated in the B horizon.

The B horizon is also the location of adsorption and desorption reactions for sulphate ions. The ability to retain SO_4^{--} is due to adsorption by soil sesquioxides and or by retention via organic material. The retention mechanism seems to be pH dependent. At LLW, Hern et al. (1985) found that when deionized water was run through the soil, sulphate was mobilized from the organic material, retained by the mineral soil (B horizon) and the result was a low level of net mobilization of S (4,2 mg/l SO_4^{--} at 40 cm). This concentration of sulphate is similar to that seen in lake and outlet water. When a solution with a high level of sulphate was added (4,1 mg/l S), soil retention seemed to increase but sulphate concentrations in soil water reached levels of 6 mg/l SO_4^{--}. The upper 12 cm of material was able to accept 0,97 g S before being unable to retain any further S.

Other ions such as chloride, show very little adsorption/desorption reactions as they travel through the soil. Chloride concentrations remained at 0,3 mg/l during the experiment.

An important question in the context of the acidification of the environment is whether the present acid neutralizing capacity of soils and surficial deposits is being decreased. Experimental acidification of soil plots was one way of obtaining some information on the question.

Rutherford et al. (1985) and Hern et al. (1985) carried out experimental acidifications at LLW with solution of pH 3,5 and 2,0. Very few effects were seen at the low level of acidification. With a pH 2,0 solution several reactions occurred which may be indicative of results expected with long term acidification. They found that:

- There was little effect on pore water pH. The soil was still able to partially neutralize the acidic water.

- There was little effect on total soil N. There was suppression of soil nitrification but this was not simply a function of soil water pH.

- Total soil S increased particularly in the B horizon.

- Leaching rates were enhanced to 17 kg/ha for Al, to 7 kg/ha for Mg, to 14 kg/ha for Ca and to 6 kg/ha for K.

- A much greater magnitude of Al mobilization, high in the profile, was seen but redeposition reduced net leaching rate.

- There appeared to be a reduced CEC and base saturation in humic layer only (table 15).

- Significant decreases in soil Fe oxides occurred just below the Ae horizon.

4.7 Groundwater

Surficial deposits are mainly till of variable thickness (figure 4). An underground valley passes below the lake and outlet which may channel water out of the watershed without entering the lake. The other portion of groundwater flow will be directed towards the lake and the average permeability of the aquifer of $1,5 \times 10^{-3}$ cm/s even makes it possible for groundwater flow to assure exclusively the recharge of the lake. Increases in the height of the watertable occur mainly in the spring and fall with decreases in the summer and winter months.

The quality of groundwater varies considerably over the watershed (table 16). For instance, alkalinity ranges from 0 to 600 µeq/l from one site to another (Bernier et al., 1983). Increases in alkalinity are accompanied by increases in pH, Ca, Mg, and Na. The differences in groundwater quality seem related to the properties of the material through which water travels as well as the residence time of water in the surficial deposits.

Table 15. The effect of experimental acidification on cation exchange capacity (mole/kg X 100) and base saturation (%) in laboratory columns (Rutherford et al., 1985).

Horizon	pH 5,7		pH 3,5		pH 2,0	
depth (cm)	CEC	BS	CEC	BS	CEC	BS
LH	20,7	(59)	21,0	(58)	15,2	(24)
Ae	1,5	(28)	2,9	(26)	1,5	(27)
15-20	3,7	(12)	4,3	(10)	2,7	(10)
20-30	3,9	(12)	3,8	(10)	4,1	(6)
30-45	3,5	(15)	3,5	(13)	3,8	(10)
45	2,5	(22)	2,9	(18)	3,1	(18)

Table 16. Groundwater quality at three depths in the Laflamme Lake Watershed.

Parameter		PIOZEMETERS P9 1,1 m			P3 4,0 m		F1 13,3 m	
		F 81	F 82	F 83	F 82	WS 83	F 81	F 82
pH		5,0	4,8	5,1	5,8	6,3	6,7	6,5
Cond.	µS/cm	43	23	27	28	29	96	80
Alk	µeq/l	89	5	10	168	199	780	577
Ca^{++}	µeq/l	115	111	130	158	180	315	320
Mg^{++}	µeq/l	41	29	30	56	58	247	246
Na^{+}	µeq/l	70	35	30	88	91	126	124
K^{+}	µeq/l	46	6	4	9	6	28	13
SO_4^{--}	µeq/l	--	110	64	67	57	--	60
NO_3^{-}	µeq/l	--	56	110	14	34	--	16
Cl^{-}	µeq/l	--	17	15	17	11	--	17
SiO_2	mg/l	--	7	6	17	16	--	15
Mn	mg/l	--	0,05	0,07	0,04	0,03	--	0,01
Al	mg/l	--	0,36	0,89	0,04	0,34	--	0,13

F : fall
W : winter
S : spring

In surface piezometers (P9), water is still acidic (pH= 5,0) with little or no alkalinity and this acidity favors high Al concentrations (0,36 - 0,89 mg/l). Water composition is dominated by $CaSO_4$. Major ion concentrations are similar to those in soil pore water (table 10). Of the groundwater components, it is the water in shallow piezometers that is the most variable and this variability depends upon the time since the last infiltration and its importance.

At a depth of 4 m (P3), alkalinity, Ca, Mg, Na, silicate and K have increased in concentration over levels at 1 m while H^+, NO_3, Al and to a lesser extent SO_4 and Mn decreased. Sulphate ions are no longer the dominant anions. The neutralization of H^+ ions which began in the soil horizons continues probably due to the weathering of silicates such as potassic feldspars and plagioclases. The weathering of silicate under this type of climate leads to the formation of kaolonite and the liberation of Ca, Na, K, Mg, Fe and the dissolution of amorphous silica. Mg and Mn can also be found in minerals such as hypersthene and magnetite.

The same trends in water quality observed at 4 m are found at the outlet, in deep piezometers, although SiO_2 values remain near 16 mg/l. The acidity of water is very low (pH = 6,6) and buffering is high. Sulphate levels are 60 µeq/l, a concentration close to predicted background levels for the Canadian Shield. Chloride ion concentrations remain the same throughout the groundwater system. Bernier et al. (1983) also found that water sampled from a swampy area had water characteristics more similar to that of deep groundwater than wells at an equivalent depth.

Changes in groundwater quality during the year are shown in figure 14. Episodic acidification of groundwater was seen in the fall of 1982 but only in shallow piezometers. Although acidification was expected to occur during spring melt, no sudden drops in pH or alkalinity were observed by Padilla et al. (1983) in the spring of 1983. This may have been due to frozen soils which might have prevented the first meltwater, usually the most acidic, from reaching the watertable.

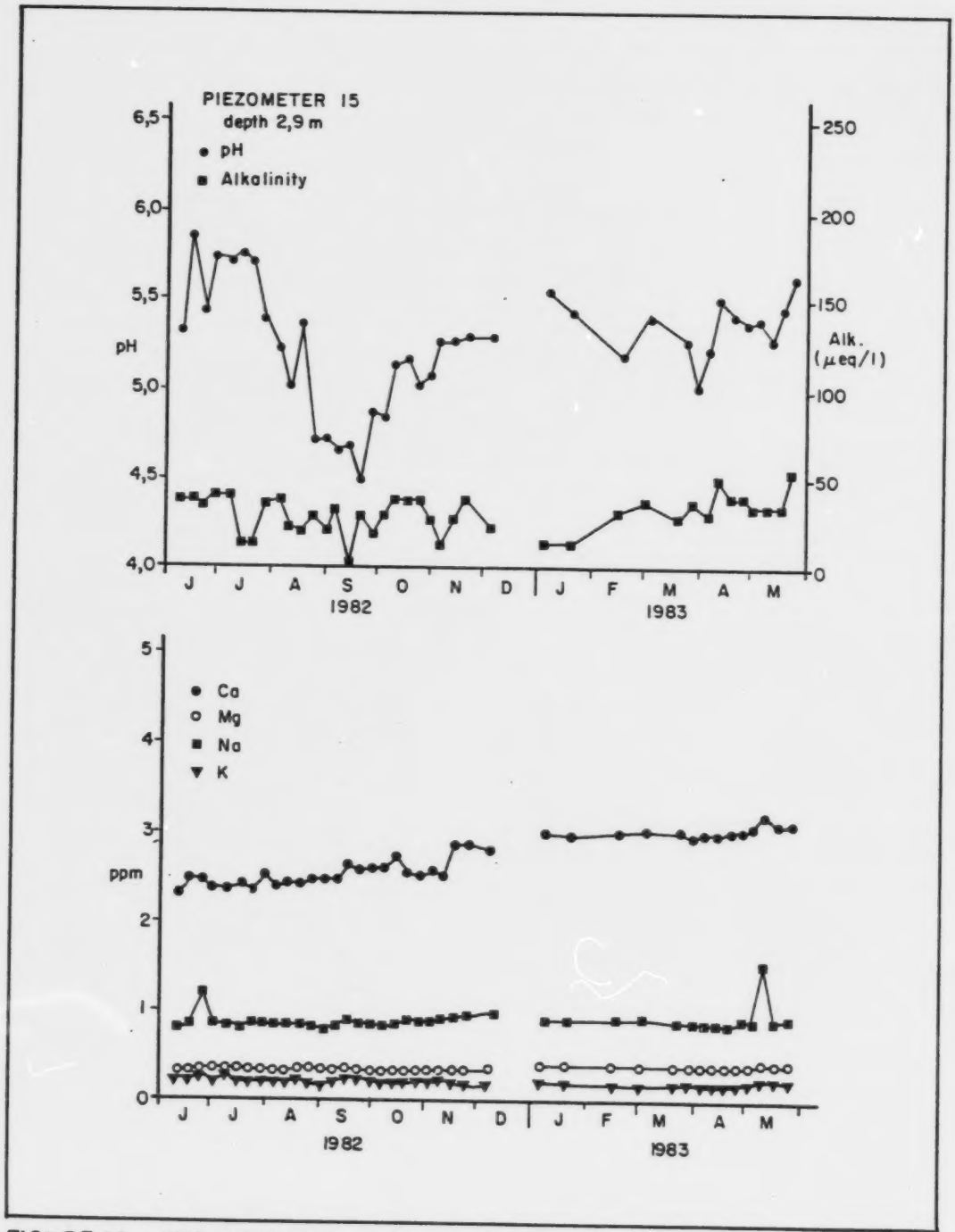

FIGURE 14 : GROUNDWATER QUALITY VARIATIONS IN THE RECHARGE AREA.
(from Padilla et al, 1984)

Water quality varies considerably between dilute acidic precipitations and deep mineralized groundwater indicating the importance of watershed processes. The chemistry of lake water will depend on partitioning of water along the various flow paths through the system. Other than the type of input, lake quality will be affected by in-lake processes and chemical lake storage.

5. LAKE AND OUTLET WATER CHEMISTRY

5.1 Field Data and Limnology

Lakes on the Laurentian Shield are usually poorly mineralized as is the case of Laflamme Lake. Conductivity ranges from 14 to 38 µS/cm with values generally increasing with depth except during periods of mixing.

The thermal regime of the lake is influenced by seasonal changes. Just before ice over in early November, there is a four to five week period when water temperature is uniform throughout the water column and temperatures decrease uniformly from 11 to 3°C (figure 15). Dissolved oxygen levels and conductivity also are distributed evenly over the water column. During the 26 weeks of ice cover, an inverse thermal stratification develops with low temperatures at the ice interface and higher temperatures at depth (4,3°C). Massive snowmelt precedes ice breakup which usually occurs in mid-May. The inverse stratification in the lake serves to concentrate acidic inflows in the upper surface waters. Most chemical changes brought about by meltwater are lost when turnover occurs. Highest temperatures at the lake surface (22°C) are reached in July and August. Temperature at a depth of 4 m are about 14°C during these two months. The maximum average water column temperature is a little over 17°C.

The ice cover isolates the lake surface from the atmosphere and oxygen concentrations decrease over the winter to oxygen saturation values as low as 5% at 4 m in late April (figure 16). This period coincides with the time of additional stress due to snowmelt. During summer months, oxygen saturation is rarely less than 50%.

5.2 Lake Storage

As mentioned earlier, lake chemistry depends on the inputs into the lake, in-lake processes and lake storage. Due to the small size of the lake,

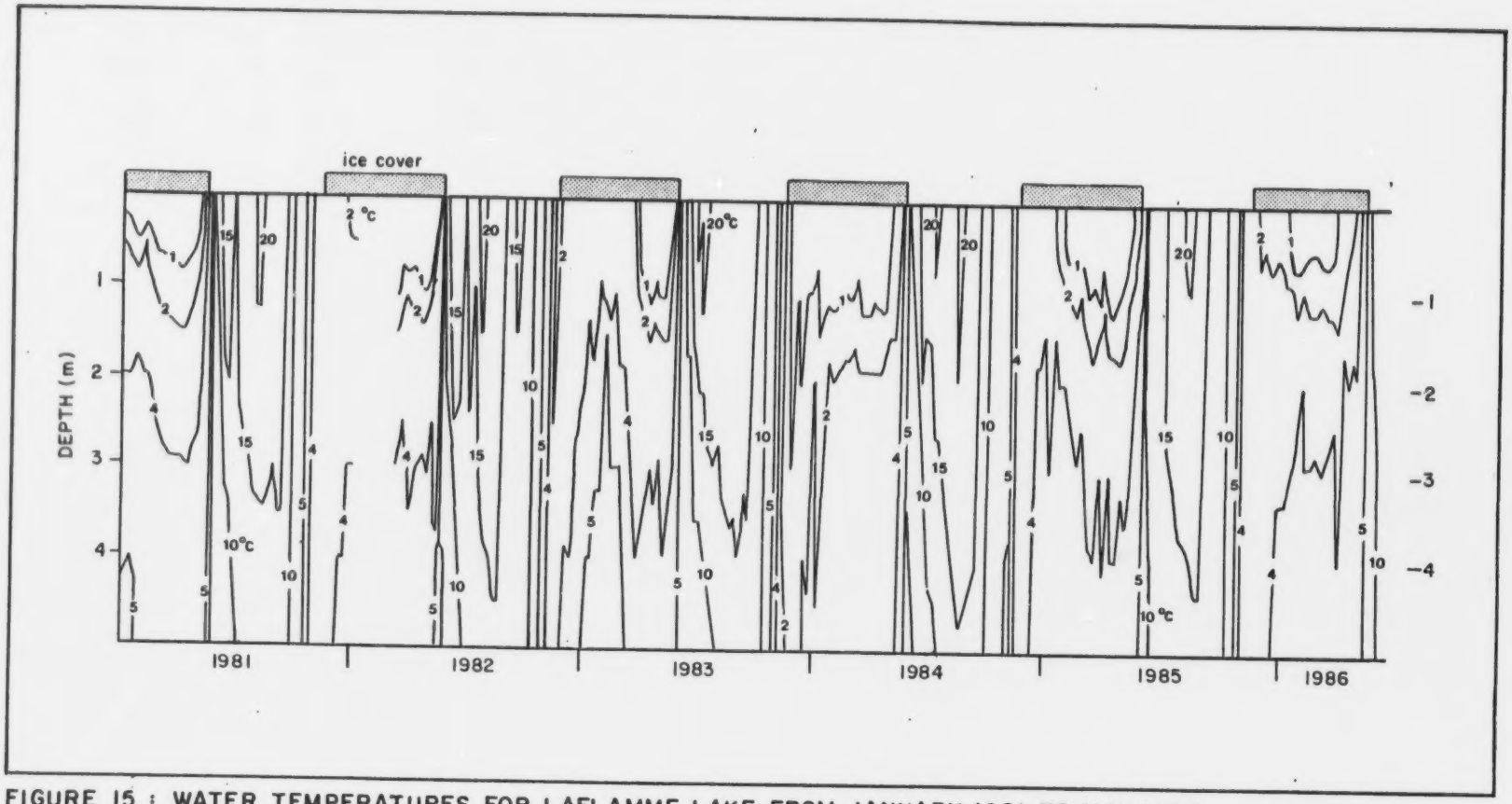

FIGURE 15 : WATER TEMPERATURES FOR LAFLAMME LAKE FROM JANUARY 1981 TO MAY 1986.

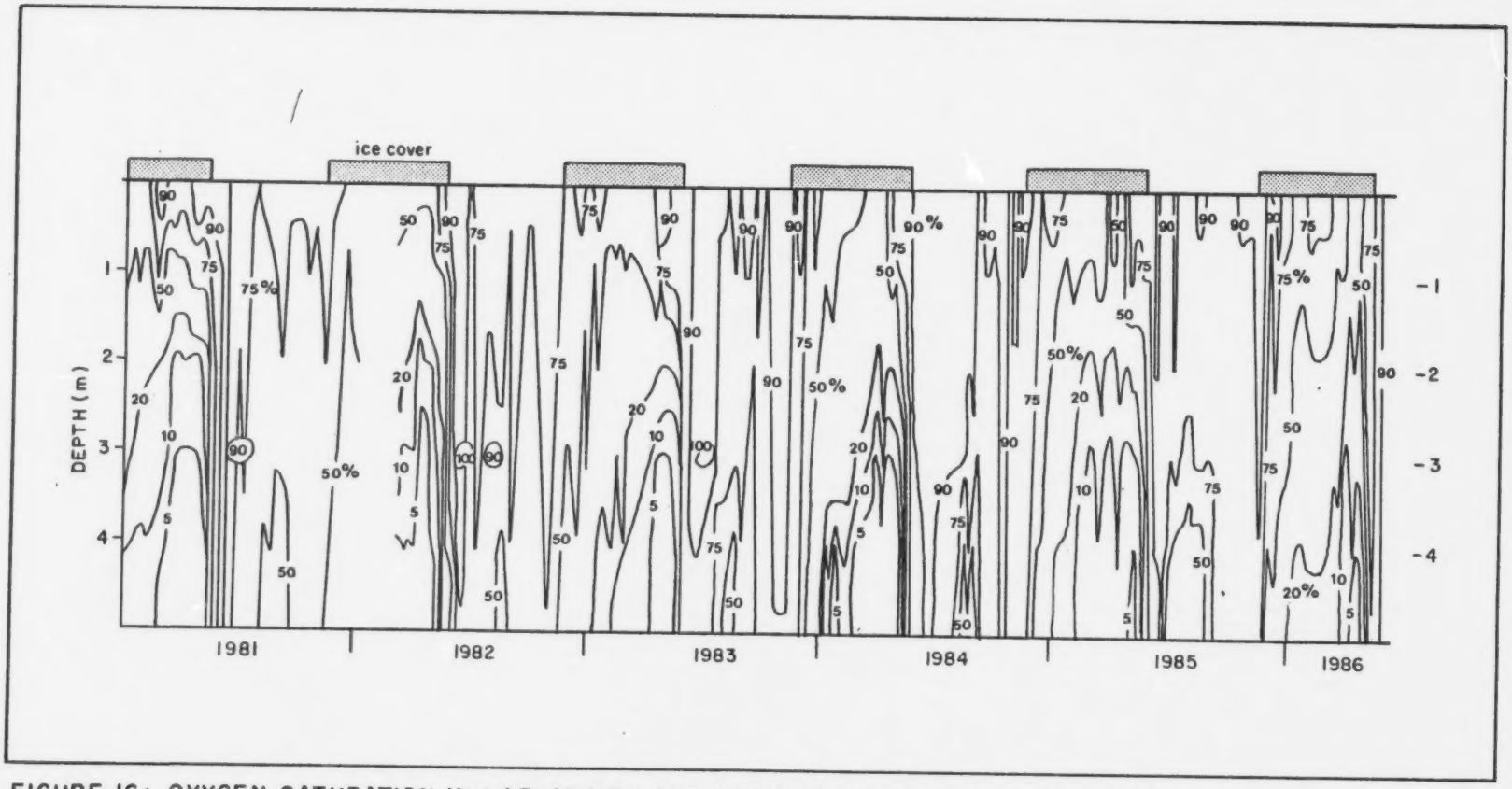

FIGURE 16: OXYGEN SATURATION IN LAFLAMME LAKE FROM JANUARY 1981 TO MAY 1986.

the amount of material stored in the lake itself is only a fraction of about 25% of the amount of material that leaves the lake each year. For the hydrogen ion the amount is even below 25%. In the case of calcium, the amount stored in the lake is about 300 kg while outflow is close to 1300 kg. Sulphate values are higher with 500 kg within the lake reservoir and a yearly output of 2300 kg. Incoming precipitation contains 1500 kg SO_4.

Lakes with a small reservoir of chemicals would be expected to be much more sensitive to changes in input than larger headwater lakes where residence times are measured in years rather than months.

5.3 Chemical Composition of Water

A description of water chemistry at the center of the lake and at the outlet for the last 5 years is given in table 17. Table 18 summarizes data for various other parameters with less complete data series.

Lake chemistry is dominated on an equivalent basis by calcium (0,123 meq/l) bicarbonate ions (0,111 meq/l) and sulphate ions (0,088 meq/l). Other chemical parameters (Na, Mg, Cl, K, NO_3, H) are present in concentrations of less than 1 mg/l. The relative composition of lake water over the last five years is given in table 19. Although the concentration of various cations changed over the years, the overall proportion of each remains quite stable with calcium, magnesium, sodium and potassium representing 57%, 20%, 19%, and 3% respectively. Hydrogen ions values are very low (< 1%).

In the case of anions, the relative importance of sulphate and bicarbonate ions is rather variable, although over the last three years they seem to have remained close to 40% and 50% respectively. Chloride (5%) and nitrate ions (4%) complete the make up. The overall cation to anion ratio shows a slight cation deficiency.

In many lakes or streams that have been acidified, the lake chemistry shifted from a calcium-bicarbonate system to a calcium-sulphate system. Although on an annual basis there is more bicarbonate than sulphate in this system, there are periods during the summer when bicarbonate ions decrease to

Table 17. Statistical descriptors for water chemistry parameters from June 1981 to May 1986.

PARAMETER		MEAN	SD	C.V.	N	MIN	MAX
LAKE							
pH	(units)	6,4	0,2	3	258	5,6	7,0
H^+	(µg/l)	0,5	0,3	58	258	0,1	2,5
Ca^{++}	(mg/l)	2,5	0,5	19	259	1,3	3,7
Mg^{++}	(mg/l)	0,5	0,1	20	259	0,3	0,8
Na^+	(mg/l)	0,9	0,2	21	259	0,4	1,6
K^+	(mg/l)	0,2	0,1	49	259	L0,1	1,0
Cl^-	(mg/l)	0,4	0,1	27	258	0,1	1,1
SO_4^{--}	(mg/l)	4,1	0,6	14	257	2,3	6,2
NO_3^-	(mgN/l)	0,11	0,11	102	255	L0,01	0,41
P	(mgP/l)	0,036	0,011	32	244	0,014	0,072
Alkalinity	(mg/l)	5,7	1,9	34	255	1,1	10,1
Conductivity	(µS/cm)	24	5,5	23	258	14	38
Colour	(units)	23	9,0	38	256	6	69
Al	(mg/l)	0,09	0,05	48	256	0,02	0,30
Fe	(mg/l)	0,13	0,06	46	256	0,01	0,44
Zn	(mg/l)	0,005	0,002	48	255	L0,001	0,012
Mn	(mg/l) *	0,020	0,009	45	52	0,008	0,039
OUTLET							
pH	(units)	6,3	0,3	5	257	5,0	6,9
H^+	(µg/l)	0,7	1,2	161	257	0,1	10,0
Ca^{++}	(mg/l)	2,3	0,5	23	257	0,8	3,8
Mg^{++}	(mg/l)	0,5	0,1	23	260	0,1	0,8
Na^+	(mg/l)	0,9	0,2	25	260	0,1	1,4
K^+	(mg/l)	0,2	0,1	58	260	L0,1	1,5
Cl^-	(mg/l)	0,4	0,1	28	258	0,1	1,0
SO_4^{--}	(mg/l)	4,2	0,6	15	258	3,0	6,2
NO_3^-	(mgN/l)	0,11	0,11	104	257	L0,01	0,45
P	(mgP/l)	0,034	0,012	34	246	0,013	0,067
Alkalinity	(mg/l)	5,0	2,2	44	254	0,3	10,4
Conductivity	(µS/cm)	23,0	5,6	25	259	12	40
Colour	(units)	23,4	9,0	39	256	7	71
Al	(mg/l)	0,10	0,05	50	257	0,04	0,34
Fe	(mg/l)	0,12	0,06	49	257	0,02	0,38
Zn	(mg/l)	0,004	0,002	49	257	L0,001	0,011
Mn	(mg/l) *	0,023	0,012	52	52	0,006	0,055

(*) Values from June 1981 to May 1982.

Table 18. Additional water quality parameters.

Trace Metals

Parameter	Range (mg/l)	% Observations above Detection Limit
Ni	< 0,001 - 0,004	7
Cu	< 0,001 - 0,012	24
Cd	< 0,001 - 0,008	2
Pb	< 0,001 - 0,003	19

LRTAP Network

Parameter	Range (mg/l)	Mean	Number of Samplings
DOC	2,0 - 5,3	3,6	6
DIC	0,4 - 2,8	1,5	6
SO_4-IC	3,65 - 4,03	3,86	6
SiO_2	3,61 - 7,60	5,39	6
N-NH_3	< 0,01 - 0,058	0,026	6

Biological (Auclair, 1981)

Parameter	Range (µg/l)	Approx. Number
Chlorophyl a	0,16 - 2,68	20
Pheaopigment	0,17 - 0,91	20

Table 19. Relative proportion of major ions in lake and outlet water.

Ion	1981 µeq/l	%	1982 µeq/l	%	1983 µeq/l	%	1984 µeq/l	%	1985 µeq/l	%	Mean µeq/l	%
LAKE												
Ca^{++}	119,7	58	130,0	58	120,9	57	120,0	57	122,6	57	122,6	57
Mg^{++}	40,9	20	44,2	20	44,3	21	43,9	21	44,2	21	43,5	20
Na^{+}	40,2	19	43,3	19	39,2	18	41,2	19	41,0	19	41,0	19
K^{+}	4,2	2	5,5	2	7,0	3	5,5	3	5,9	3	5,6	3
H^{+}	1,8	1	0,6	-	0,6	-	0,5	-	0,5	-	0,8	-
HCO_3^-	91,8	44	134,7	57	107,8	51	110,0	51	109,9	49	110,8	51
SO_4^{--}	96,6	46	77,7	33	84,2	40	85,7	40	83,4	42	87,5	40
Cl^-	11,3	5	12,5	5	11,9	5	11,3	5	12,1	5	11,8	5
NO_3^-	8,7	4	9,8	4	8,9	4	7,6	4	7,2	3	8,4	4
Cations	206,8		223,6		212,0		211,1		214,1		213,5	
Anions	208,4		234,7		212,8		214,6		222,5		218,5	
% DIFF	-0,7		-4,8		-0,4		-1,6		-3,9		-2,3	

Ion	1982 µeq/l	%	1983 µeq/l	%	1984 µeq/l	%	1985 µeq/l	%	Mean µeq/l	%
OUTLET										
Ca^{++}	123	58	110	57	113	58	122	58	117	57
Mg^{++}	41	19	39	20	40	20	43	20	41	20
Na^{+}	42	20	36	19	38	19	40	19	39	19
K^{+}	5	2	7	4	4	2	6	3	6	3
H^{+}	0,8	-	0,9	-	0,6	-	0,7	-	0,8	-
HCO_3^-	118	54	90	46	96	48	102	47	102	48
SO_4^{--}	79	36	86	44	88	44	98	45	88	42
Cl^-	13	6	12	6	10	5	11	5	12	6
NO_3^-	10	4	9	4	7	3	7	3	8	4
Cations	212		192		196		210		204	
Anions	220		197		201		217		210	
% DIFF	-1,9		-2,6		-1,4		-3,1		-2,9	

the point that sulphate is the dominant ion in the system. Even in periods when sulphate values are below bicarbonate ion values, it does not mean that the system is not affected by atmospheric acid loading. Harvey et al. (1981) consider that 60 µeq/l is the maximum value for natural sulphates in surface water on the Canadian Shield due to the fact that rocks containing sulfur are almost absent from the shield. Exceeding sulphates would come from man-made sources.

At the outlet, the relative importance of cations is similar to the distribution found in the lake even if values of calcium, magnesium and sodium are slightly lower in stream water. Concentration of bicarbonate ions are also lower in the stream than in the lake while the reverse is true for sulphate and hydrogen ions. At the outlet, since 1983, the relative importance of bicarbonate and sulphate ions are both close to 45%. Streamflow seems to be less mineralized (-6%) and slightly more acidic than lake water with higher concentrations of aluminum and manganese. In fact, stream water chemistry tends to reflect more closely the chemistry of the upper 2 m of the lake rather than the chemistry of the entire reservoir.

The range of variation of major ions during the five year period is given in table 17. Many parameters show pronounced seasonal cycles or sharp changes which can be associated with changes in water hydrology (spring melt, fall storms) changes in biological activity and with increased acid loading to the lake or outlet.

Changes in water chemistry are usually more pronounced at the outlet than in the integrated sample at the centre of the lake although the patterns of change are similar. In this section, chemical changes at the outlet will be illustrated. The same type of information on lake water has been published in Papineau (1983, 1984, 1985).

5.3.1 Alkalinity, Calcium, Magnesium, Sodium and Conductivity.

Parameters associated with weathering such as calcium, magnesium, sodium, silica, conductivity and alkalinity have the same overall behaviour in

LLW (figure 17). Concentrations are high in winter due to slow flowing groundwater recharge and decrease rapidly with spring melt dilution. The concentrations remain below average in the summer and gradually increase in the fall when flow rate and biological activity decrease. Important water inputs in the fall or during midwinter thaws decrease the concentrations of weathering parameters.

Added to decreases in alkalinity brought about by dilution, values will decrease when used to neutralize incoming acidic water. At the outlet alkalinity values as low as 0,3 mg/l $CaCO_3$ or 6 µeq/l were measured during spring melt while winter values averaged 150 µeq/l. In comparison, during the heavy rains of the fall of 1982, alkalinity decreased to values of 46 µeq/l.

Correlations between calcium, magnesium, sodium and alkalinity are strong with coefficients (r) above 0,7 (figure 18, table 20). This indicates that over 50% of a given value can be explained by the alternate parameter. This group of parameters is also highly correlated to conductivity and nitrate ions in lakewater. There also exists a relation with iron, phosphorus and colour. There is a low, but significant negative relation between sulphate and bicarbonate ions in lake water but not at the outlet. There does not seem to be any relation between weathering parameters and potassium or pH. Conductivity relates to other parameters in much the same way as calcium, magnesium, sodium and alkalinity except for the colour relation.

Conductivity is the only parameter of this group that had a significant regression coefficient when statistical analysis was carried out against time. Values increased at the outlet (+3,7) and in the lake (+3,3) (table 21).

5.3.2 Phosphorus, Nitrate, pH and Colour

These four parameters also show seasonal cycles (figure 19). Phosphorus and nitrate ions follow the same general pattern as that of weathering elements.

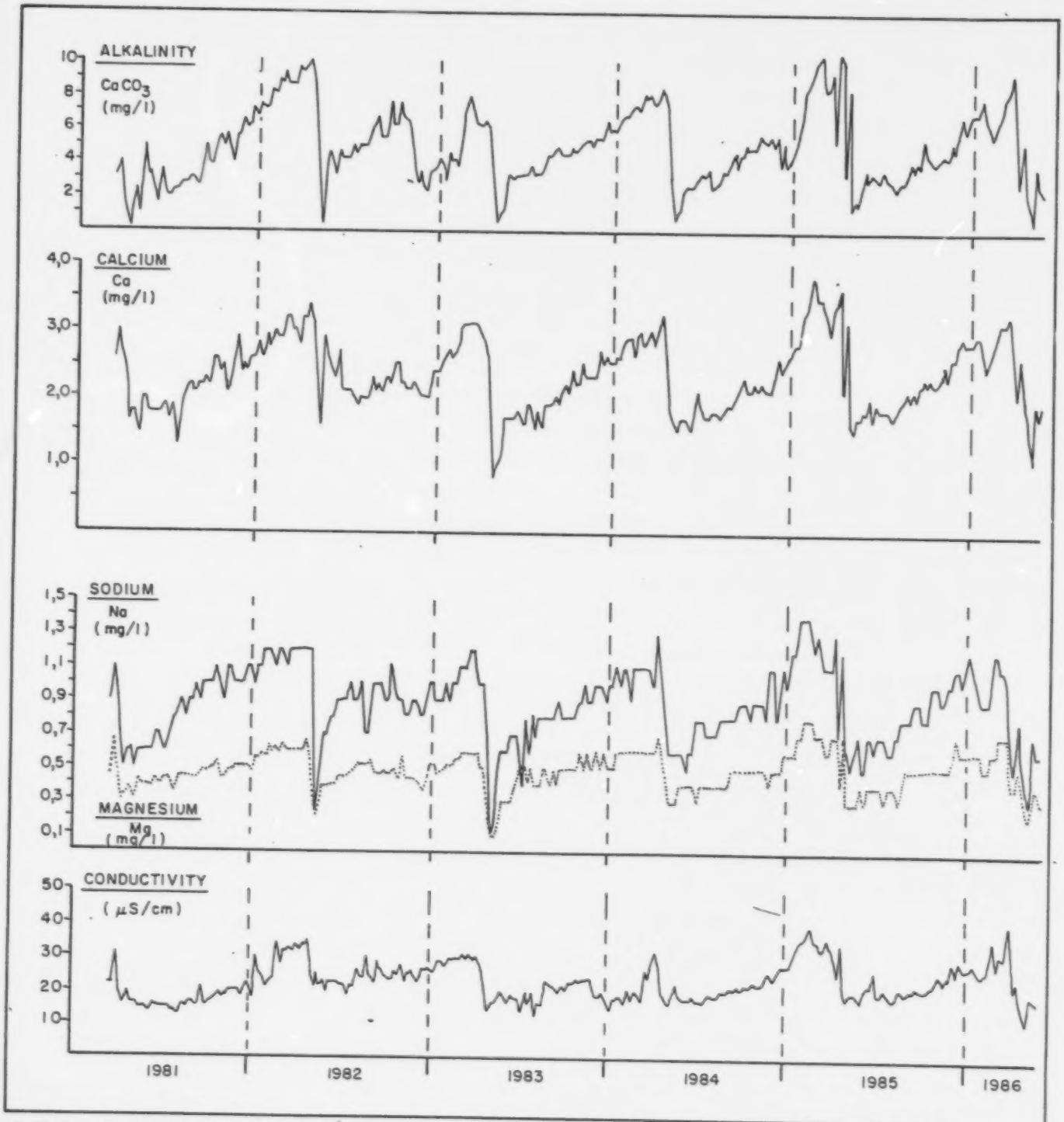

FIGURE 17: CHEMICAL VARIATIONS IN WATER ALKALINITY, CALCIUM, SODIUM, MAGNESIUM AND CONDUCTIVITY AT LAFLAMME LAKE OUTLET (MARCH 1981 – MAY 1986).

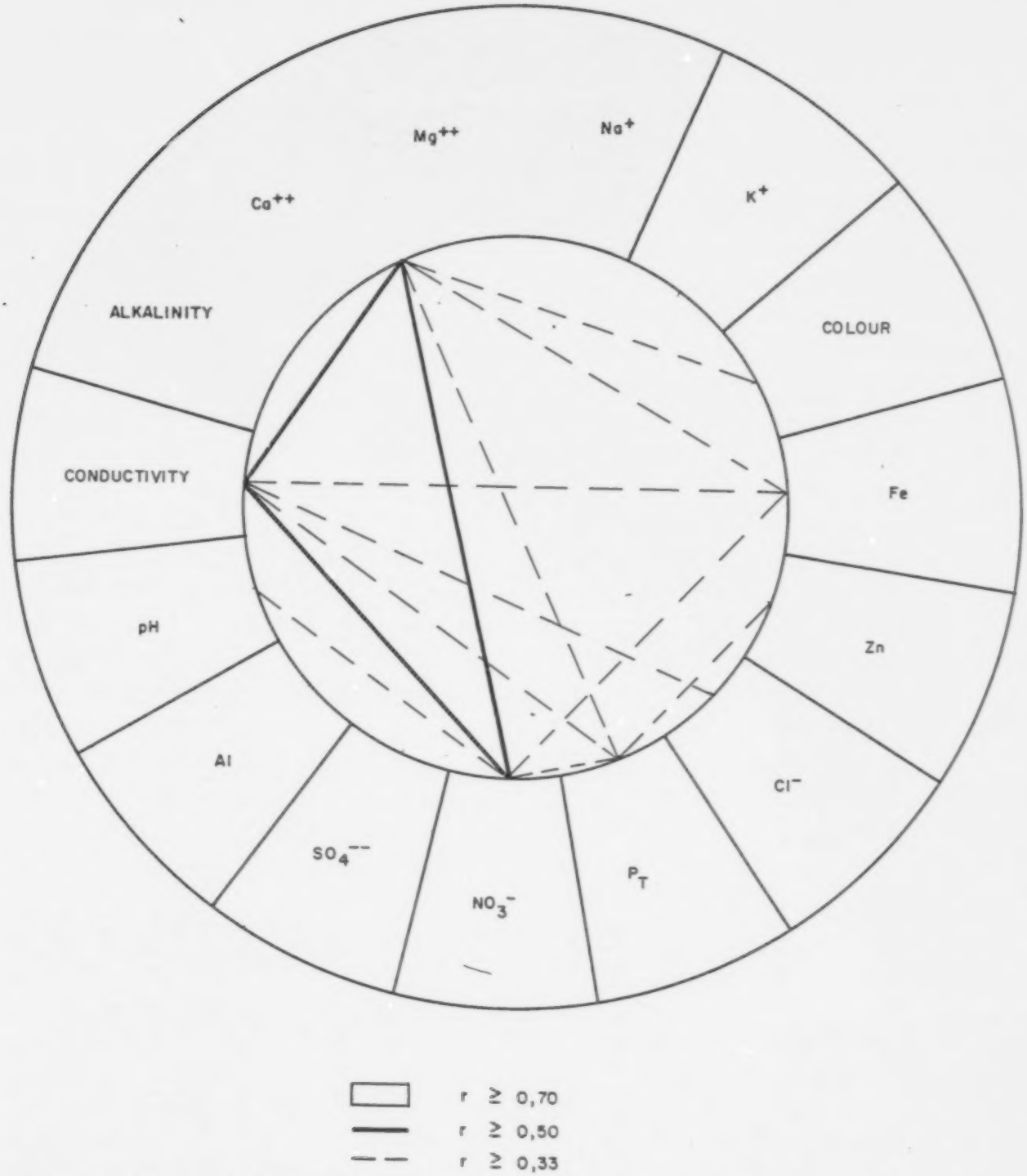

FIGURE 18 : CORRELATIONS BETWEEN WATER QUALITY PARAMETERS IN THE LAKE (JUNE 1981 – MAY 1986).

Table 20. Correlation matrix for water quality parameters at the outlet.

	pH	Ca	Mg	Na	K	Alk	SO_4	Cl	NO_3	P	Cond	Col	Al	Fe	Zn
pH	*														
Ca	0,17	*													
Mg	0,35	0,88	*												
Na	0,27	0,86	0,86	*											
K	-0,42		-0,15	-0,21	*										
Alk	0,26	0,87	0,86	0,84		*									
SO_4			0,16		-0,16		*								
Cl		0,17		0,15	0,17	0,16		*							
NO_3	-0,43	0,39	0,18	0,21	0,24	0,21		0,13	*						
P		0,55	0,46	0,48		0,47	0,14		0,22	*					
Cond		0,74	0,68	0,63		0,68	0,19	0,23	0,47	0,46	*				
Col	-0,15	-0,43	-0,47	-0,49	0,19	-0,39	-0,14	0,14	-0,20	-0,24	-0,28	*			
Al	-0,17		-0,15	-0,17		-0,21	0,15	0,20		0,20		0,15	*		
Fe		0,56	0,52	0,43	0,13	0,55			0,35	0,28	0,62	-0,16		*	
Zn	-0,16	0,12			0,13		0,22		0,26				0,29		*

Critical value (2 tail, 0,05) = ± 0,12168 N = 260

Table 21. Regression of water quality parameters versus time from June 1981 to May 1986.

PARAMETER		$\bar{X}$	CTE	r	α	5 YEARS
LAKE						
pH		6,35	6,30	0,12	0,05	+ 0,09
Alk	mg/l	5,66	5,66	0,002	NS	+ 0,02
Ca^{++}	mg/l	2,46	2,45	0,02	NS	+ 0,03
SO_4^{--}	mg/l	4,10	3,81	0,29	0,001	+ 0,57
NO_3^-	mgN/l	0,11	0,11	-0,04	NS	- 0,01
Cond	μS/cm	24,4	22,4	0,17	0,004	+ 3,3
K^+	mg/l	0,23	0,19	0,18	0,004	+ 0,07
Cl^-	mg/l	0,42	0,38	0,15	0,02	+ 0,06
Fe	mg/l	0,128	0,088	0,34	0,001	+ 0,068
Zn	mg/l	0,005	0,004	0,24	0,001	+ 0,002
OUTLET						
pH		6,30	6,27	0,07	NS	+ 0,07
Alk	mg/l	4,99	5,10	-0,03	NS	- 0,2
Ca^{++}	mg/l	2,32	2,30	0,03	NS	+ 0,05
SO_4^{--}	mg/l	4,19	3,82	0,31	0,001	+ 0,73
NO_3^-	mgN/l	0,11	0,11	-0,04	NS	- 0,01
Cond	μS/cm	23	21	0,19	0,002	+ 3,7
Al	mg/l	0,104	0,091	0,14	0,02	+ 0,026
Fe	mg/l	0,121	0,096	0,25	0,001	+ 0,050
Zn	mg/l	0,0039	0,0035	0,13	0,04	+ 0,0008

NS : not significant

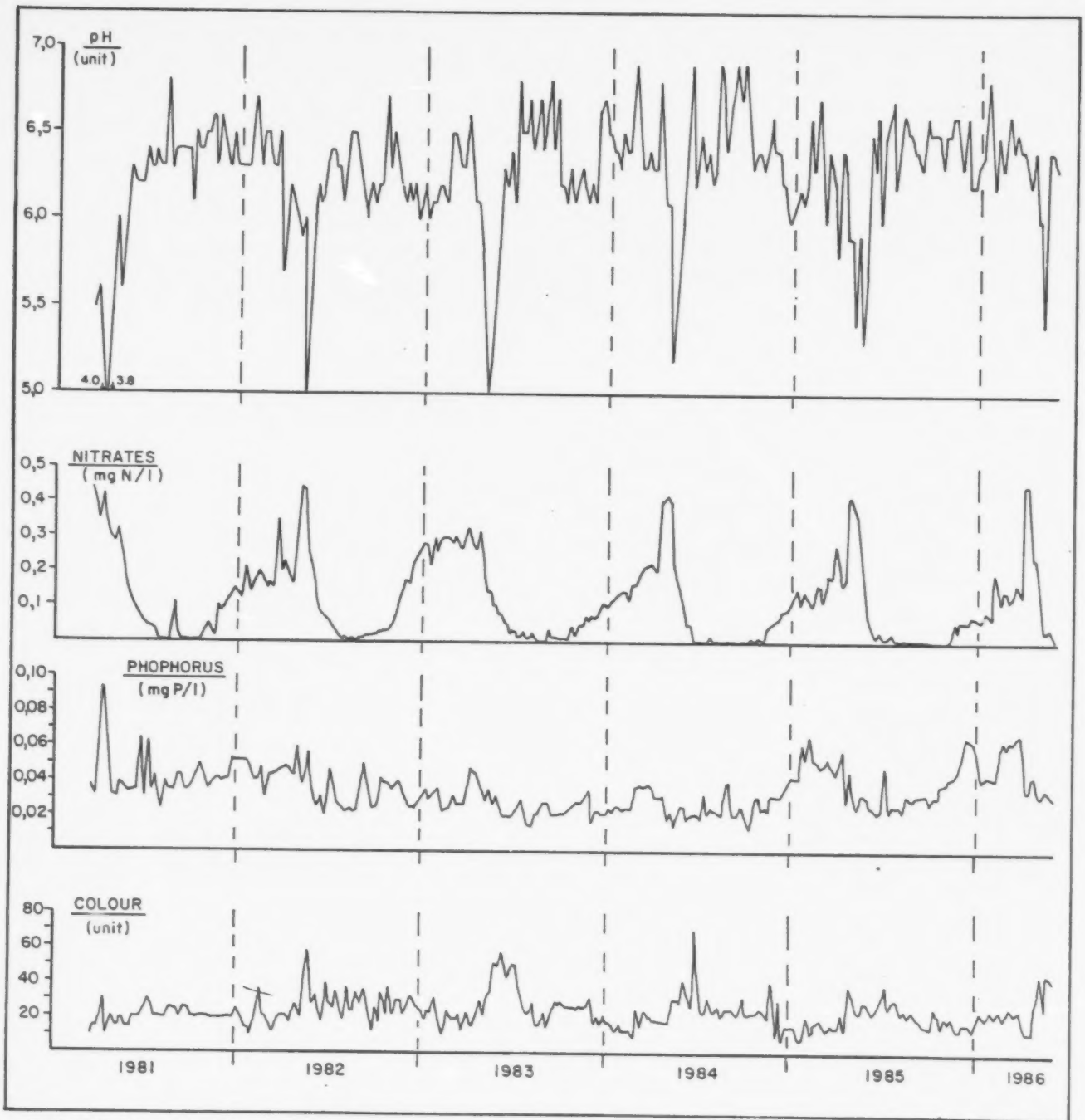

FIGURE 19 : CHEMICAL VARIATIONS IN WATER pH, NITRATES, PHOSPHORUS AND COLOUR AT LAFLAMME LAKE OUTLET (MARCH 1981 – MAY 1986).

The basic phosphorus cycle is quite clear in 1985. Unlike the other weathering element cycles, there is a transient decrease in otherwise high winter values in and about the month of January lasting from 6 to 15 weeks. There are also spikes which usually follow the lower inflexion point of the curve in summer.

The nitrate cycle reflects the important biological assimilation of this element when temperatures increase in the system. During the fall, values steadily increase. In the spring, concentration changes are not dictated by simple dilution as with calcium. In fact, during several years, when weathering parameters are at minimum values during spring melt, nitrate values can be quite high. This is due to a combination of low biological activity and inputs of nitrate ions from highly concentrated meltwater into the system. This pulse of nitrate is not seen every year (J.-Y. Charette, personal communication).

Spring melt also causes increases in hydrogen ion in the system which are more pronounced at the outlet than in the lake. This is caused by the fact that meltwater often only affects the top layers of the lake because of thermal stratification. pH depression in the top portion of the lake can be very important (figure 20). Values as low as 4,2 have been measured near the lake shores during the spring. The outlet pH usually decreases to values between 5,0 and 5,4 while lake column pH is closer to 5,8 except in 1981. From June 1981 to May 1986, with regression analysis, there seems to have been a slight increase in pH values but this increase is less than 0,1 units (table 21).

Colour values are usually high in May and June and then decrease over the summer to reach minimum values in January. The colour of water is usually attributable to the presence of natural mineral components such as iron and manganese and organic sources such as humic substances, tannins and lignins products of decaying vegetation. In 1982, 1983, 1984 and 1986, maximum colour readings were reached after peak discharged was recorded in the system. Colour values in 1981 do not follow the same pattern.

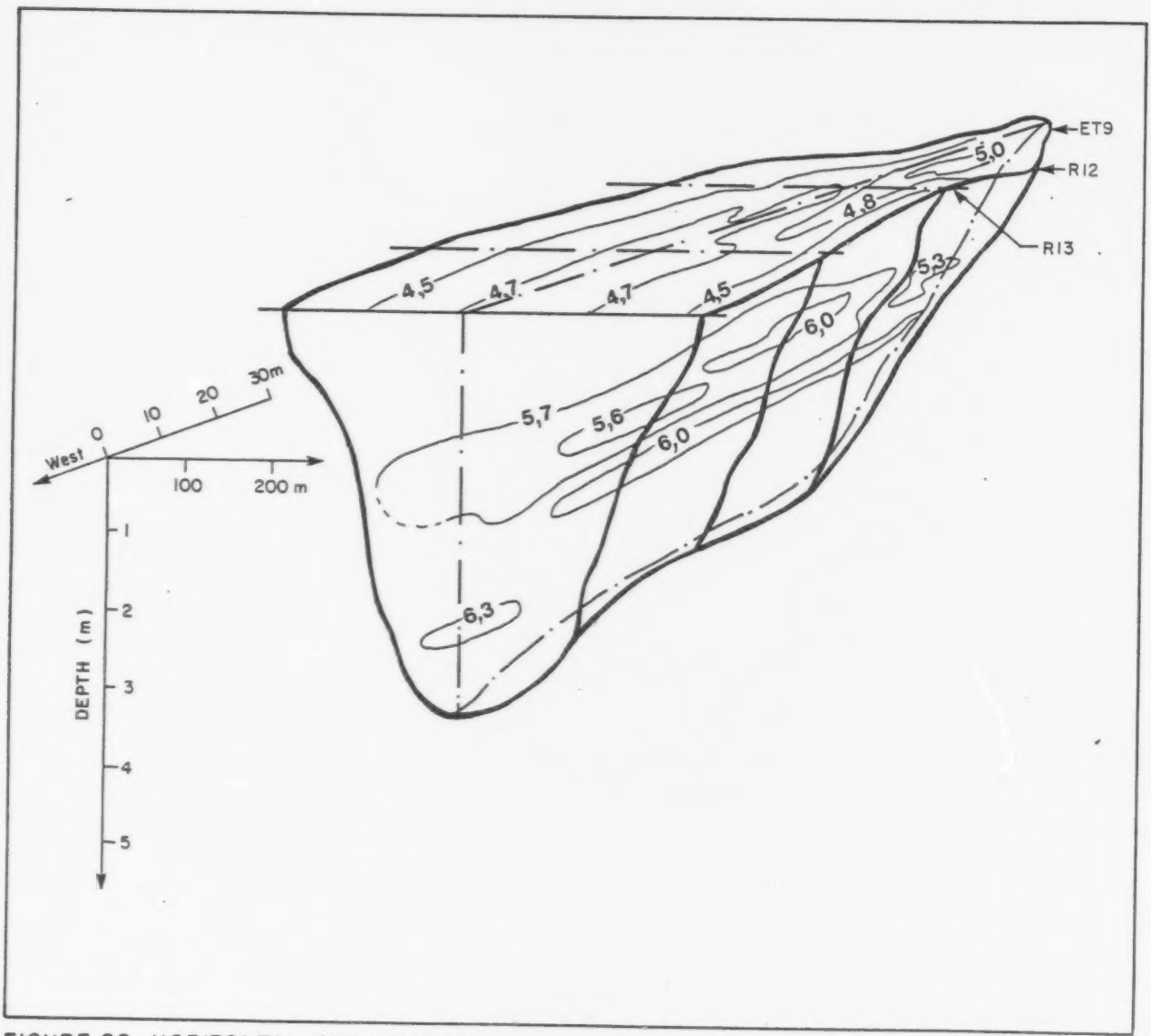

FIGURE 20: HORIZONTAL AND VERTICAL DISTRIBUTION OF pH IN LAFLAMME LAKE ON MAY 1st 1983 (FROM JONES et al 1984).

5.3.3 Iron, Zinc and Aluminum

Seasonal cycles seem much less pronounced for heavy metals such as iron, zinc and aluminum (figure 21). Changes and cycles in manganese concentrations over the study period are rather difficult to determine as the analytical method and corresponding detection limit were changed very often. However, concentrations for 1982 and 1984 are shown in figure 22. A point to keep in mind when looking at these series is the change of analytical laboratories in April 1983.

Of the three heavy metals, iron shows the highest correlation with weathering elements, conductivity and nitrate ions. Concentrations are high in winter and early spring and low in July and August. For zinc, there is a relation with phosphorus in lake water (figure 18).

Aluminum values do not seem to be correlated strongly to any other measured parameter in the system. Values seem to vary in a stepwise manner with pronounced changes in May 1982, April 1983, April 1984 and May 1985. Aluminum levels were high during the high flow period of the fall of 1982. Studies in the Adirondacks (Schofield et al., 1985) found that total aluminum concentrations were highest during periods of increased discharge. During baseflow periods total aluminum decreased. Hendershot et al. (1986) also found that Al concentrations increased with the first major spring flush but concentrations then decreased if discharge remained high. A subsequent increase was attributed to increases in soil temperature and degradation processes.

The source of aluminum in surface water is usually from soil alumino silicates and various types of aluminum hydroxides. Its solubilisation and transport depend on the presence of various components (H, NO_3, SO_4, organic matter). The fluxes of Fe and Mn are also to various degrees dependent on the same parameters. Schofield et al. (1985) who observed elevated inorganic Al levels and increases in nitrates during shifts from groundwater flow to shallow interflow, suggested that HNO_3 derived from the snowpack and nitrification in the soils, triggers acidification and Al

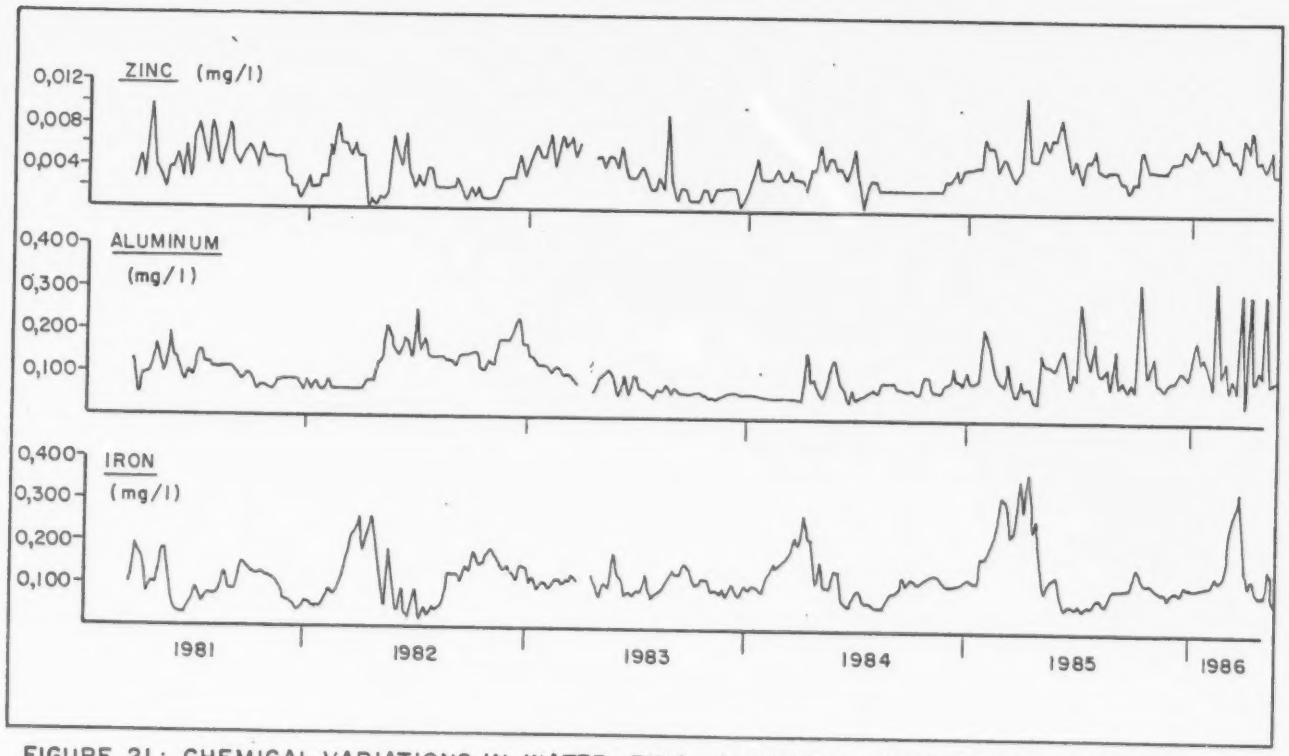

FIGURE 21 : CHEMICAL VARIATIONS IN WATER ZINC, ALUMINUM AND IRON AT LAFLAMME LAKE OUTLET (MARCH 1981 - MAY 1986).

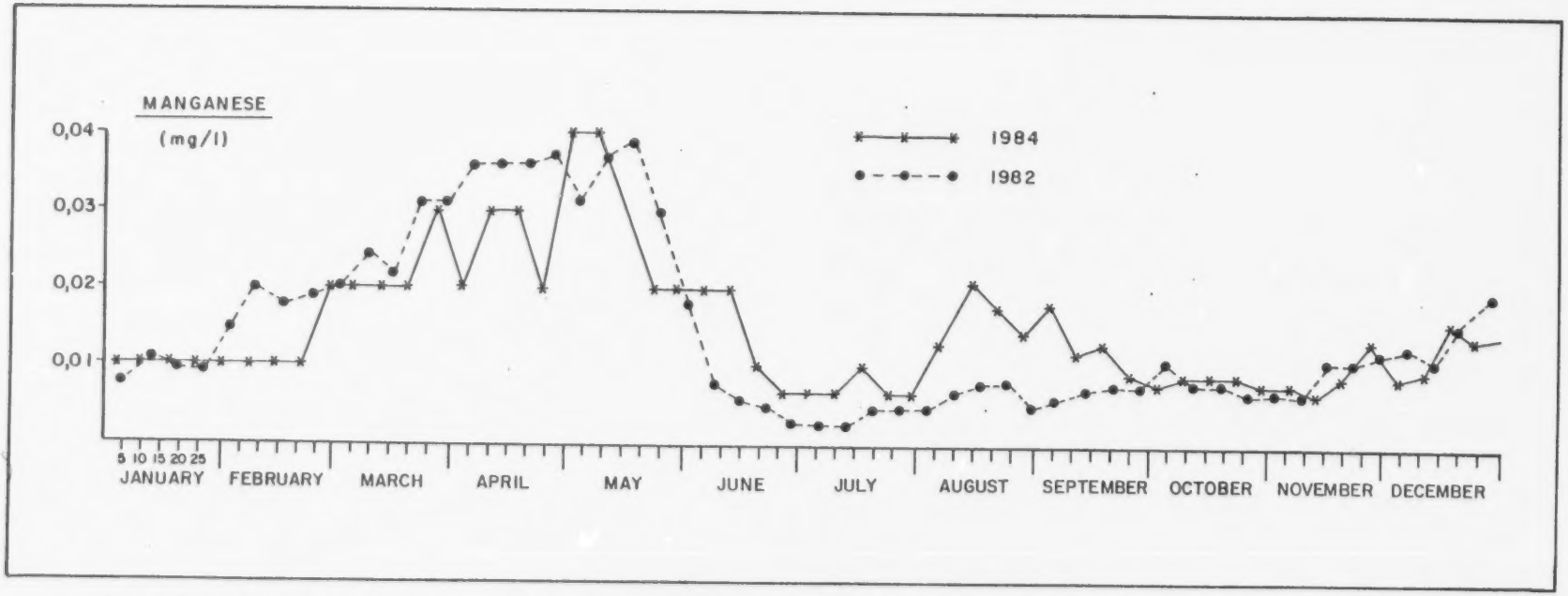

FIGURE 22: CHEMICAL VARIATION IN MANGANESE CONCENTRATION IN LAKE WATER FOR 1982 AND 1984.

mobilization. Once immobilized in the upper soil horizons, re-precipitation of Al in the B horizon may occur. Aluminum levels can also be lowered by sedimentation in the lake itself.

Aluminum concentrations are particularly important in the acidification problem since certain chemical forms of dissolved Al exert toxic effects on freshwater fish (Baker and Schofield, 1980).

Although no data exists for metal deposition in LLW, estimates from Foster and Nicholson (1986) for the Turkey Lakes Watershed in Ontario are: Fe 647, Al 351, Mn 45, Cu 41 and Pb 25 g ha^{-1} yr^{-1}. Average annual concentrations in precipitation of Fe, Al and Mn are 0,052, 0,028 and 0,005 mg/l. At the same site, leaching of vegetation increased concentrations of Mn and Cu. Soil solution was further enriched in metals especially Al from the forest floor and the mineral soil. Most of the metals leached from the rooting zone were retained in the watershed and did not appear in stream water. Low fluxes in stream water probably reflect the reduced solubility of free trace metal ions at higher pH. A net watershed gain occurred for all trace metals.

Changes in heavy metal concentrations over the study period are seen for both iron and zinc in the lake and in outlet water. Aluminum showed a statistically significant increase only at the outlet. Since a change in analytical laboratories occurred in April 1983, the Burlington series were also tested separately. In the second analysis, increases in aluminum are significant at both sites while increases in iron concentrations are no longer significant below $\alpha = 0,08$.

5.3.4 Chloride, Sulphate and Potassium Ions.

These three parameters show very little seasonality (figure 23) and show no strong correlation with other water quality parameters except for a relation between potassium and pH at the outlet and conductivity and chloride in the lake.

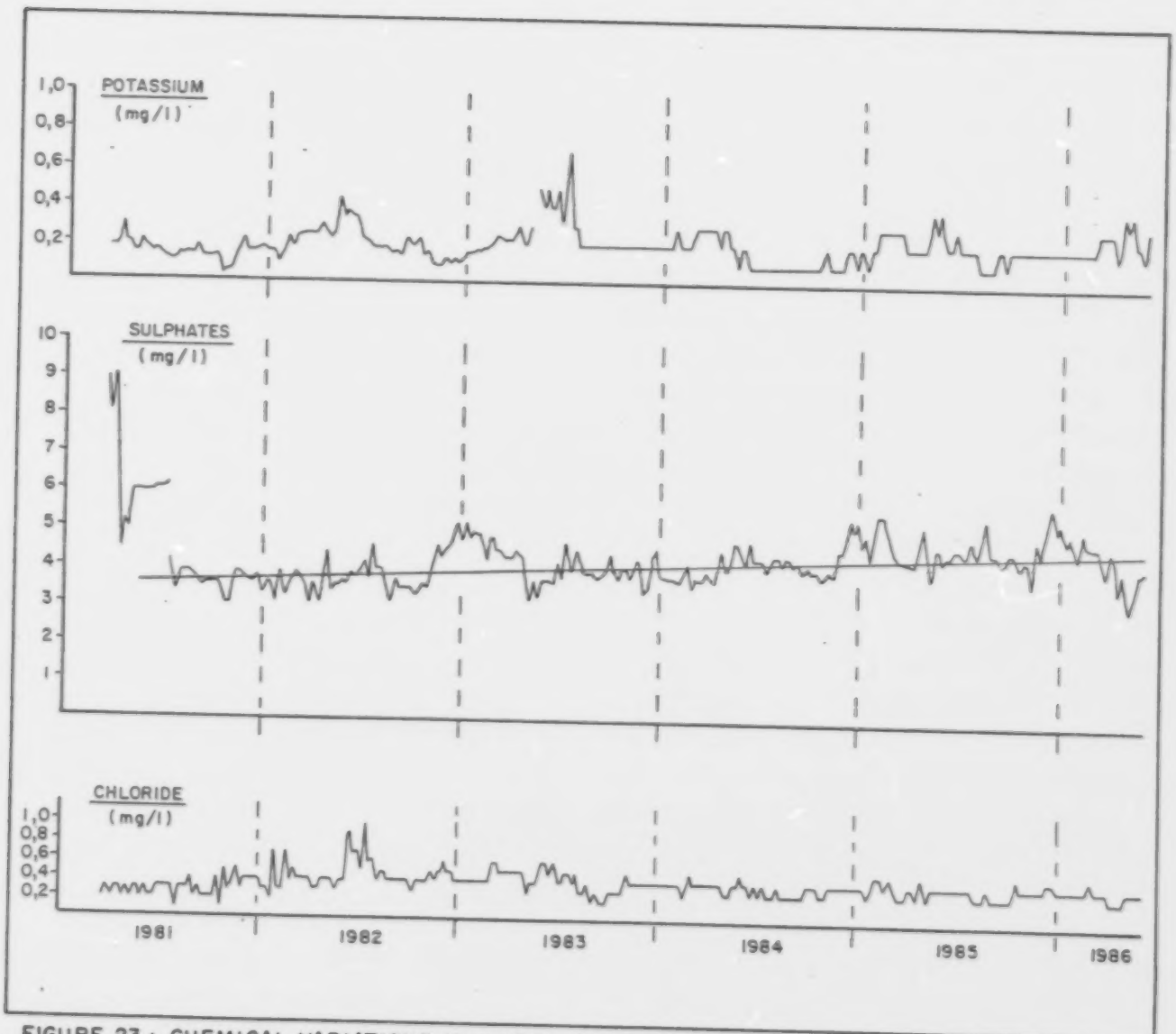

FIGURE 23 : CHEMICAL VARIATIONS IN WATER POTASSIUM ,SULPHATES AND CHLORIDE AT LAFLAMME LAKE OUTLET (MARCH 1981 – MAY 1986).

Chloride ions are considered to hardly participate in any biological or chemical process in the soil except for some minor uptake by plants. It is therefore often referred to as a conservative ion. Throughfall and groundwater values are about 17 µeq/l while precipitation and snowpack values (2-9 µeq/l) are about half the amount. Lake values range from 3 to 31 µeq/l with an average of 12 µeq/l. An important increase in chloride concentrations occurred in June and July of 1982 which can not be fully explained by rates of atmospheric loading. Chloride concentrations varied very slightly over the study period.

Potassium values averaged 0,2 mg/l. There have been a few very high, usually ponctual, values measured for this parameter almost every year during April or May but not always at both the lake and the outlet. The sampling frequency may be partly responsible for this inconsistency from year to year and site to site. Since potassium values are relatively high in litter and debris from vegetation found on the forest floor, the pattern of potassium variation might reflect different inputs of surface runoff from one spring to another. Potassium value increases since June 1981 are of the same magnitude as those of chloride ions.

Of all parameters, sulphate ions show the most pronounced increase over the study period (table 21). Values have increased by 0,6 mg/l (12 µeq/l) in lake water and by 0,7 mg/l (15 µeq/l) at the outlet. Values at the begining of the sampling program in 1981 were not considered as they seem unrealistically high. The combination of very little background chemistry on the watershed and the very particular nature of the 1981 winter and spring melt episodes in which pronounced pH depressions occurred and fish kill was noted (Verreault and Langlois, 1984) makes it quite difficult to evaluate levels of sulphate that could be considered acceptable. In a study by Jones and Bisson (1980), levels of 4,7 mg/l were measured in the lake in the winter of 1980 and values fell to 3,2 mg/l after the first melt on April 22, 1980.

In the overall trend of increase, levels rose to 4 mg/l in November 1982 and rose to 4,5 mg/l in December 1985. The November 1982 increase was accompanied by a decrease in alkalinity values in the system. Increased

levels of sulphate over time are accompanied by increase in conductivity but very little else. Increases in cations or decreases in anions, which would be required to maintain charge balance, do not seem to have occurred during this five year period. The overall sum of cations increased by about 3 µeq/l while the sum of anions increased by about 11 µeq/l. This leaves a difference of 8 µeq/l.

Factors that have not been considered in charge balance equations are the contribution of heavy metals to positive charge and the contribution of organic anions to negative charge.

The charge associated with heavy metals is not necessarily directly related to total concentration. For metal such as aluminum, only part of the total levels will contribute to the positive charge, the rest being complexed with organic or inorganic ligands. Very little work has been done on metal speciation in LLW. Jones et al. (1984), did measure levels of Al and Mn in the spring of 1983 and obtained theoretical values for free Al. In inlet streams, values ranged from 0,1 to 40 µeq/l Al and from 0,2 to 6 µeq/l Mn. Values were lower in lake water and at the outlet with ranges of 0,1 to 8 µeq/l Al and of 0,2 to 2,4 µeq/l Mn. The average total concentrations of both parameters in lake water during this period were 0,083 mg/l Al and 0,036 mg/l Mn.

The charge associated with Al is thus closer to +1 than +3 in this system. If the assumption is then made that all Mn is present as Mn^{++} and the same holds true for Zn and Fe, the total contribution of these four metals would be about 7 µeq/l (Al: 1,5 Mn: 0,7 Zn: 0,2 and Fe: 4,6 µeq/l). The contribution of these cations would have to have doubled to compensate increases in sulphate.

As there exists a relationship between organic anions and colour, changes in water colour may be a fast means of identifying possible decreases in organic ions to offset increases in sulphate ions. No such decrease in water colour occurred. So, to estimate the contribution of organic anions (A^-), the Oliver formula (1981) was applied to bi-monthly DOC data.

A^- values obtained ranged from 19 to 47 µeq/l (Gélineau and Papineau, 1986). Recent work by R. Bourbonnière indicates that values obtained by the Oliver formula might be twice the actual values of organic anions in a sample. Charge balance and differences between colorimetric and chromatographic determinations of sulphate would also be more consistent with values of 10 to 15 µeq/l A^- in LLW. Decreases would have to be important to compensate sulphate increases and maintain charge balance. What is probably occurring in the watershed is a series of small changes accompanying sulphate increases.

Sulphate isotopic studies and paleolimnological studies have been carried out in the watershed and can provide additional information on changes in surface water chemistry.

5.4 Sulphate Isotope Studies

Isotope studies were carried out to verify if anthropogenic sources were the major source of sulphate in six undeveloped watersheds (Caron et al., 1986). They were also used to gain an understanding on the location of sulphate reactions in LLW (Gélineau, 1987).

The similar δ 34 S values of sulphate in both precipitation and lake water suggested that precipitation was the main source of sulphate for Laflamme Lake (table 22). However, other sources of sulphate can not be excluded because their δ 34 S may overlap with the above values.

Table 22. Isotopic ratios in sulphate ions and water for Laflamme Lake.

	Precipitation	Lake
δ 18 O SO_4	8 to 13‰	2 to 6 ‰
δ 34 S SO_4	3 to 7‰	3 to 6 ‰
δ 18 O H_2O	-10 to -17,5 ‰	

The behaviour of δ 18 O of sulphate can only be explained as a chemical and isotopic modification (probably a biological reduction followed by a reoxidation of sulfur) of the ion possibly in the forest floor or in groundwater. Caron et al. (1986) estimated that between one third and one half of deposited sulphate can undergo this process in Quebec lakes.

Gélineau (1987) found that δ 34 S of sulphate in precipitation, inlet, lake and groundwater ranged from 3,0 to 5,4 during the summer and fall of 1986. The δ 18 O of sulphate however ranged from 8 to 12 in precipitation and from 1,0 to 4,0 in the soil, groundwater, inlet and lakewater. The contact with the forest floor seemed to be the location of important isotopic changes in sulphate ions.

5.5 Sediment Studies

The history of the lake was studied by using paleolimnological techniques. In a first study, Ouellet and Dickman (1980) saw no dramatic increase in acidobiontic algal species in recent sediments (0 - 30 cm) although some acidophilic taxa did become more numerous. The infered pH profil obtained by Dixit et al. (1987), in a later study of core diatoms, also indicated that over the time span of the core, the pH of the lake remained between 6,3 and 6,5 (figure 24).

As for the chemistry of the sediments, elements that have increased in the last 12 cm (since 1940) include lead, nickel, cadmium and sulphate or sulfur. Ouellet (1980) also found increases in zinc, iron, copper and mercury and slight decreases in aluminum and calcium and no change in pH, carbon and magnesium. Dixit et al. (1987) on the other hand found no change in iron, manganese, zinc, copper and aluminum.

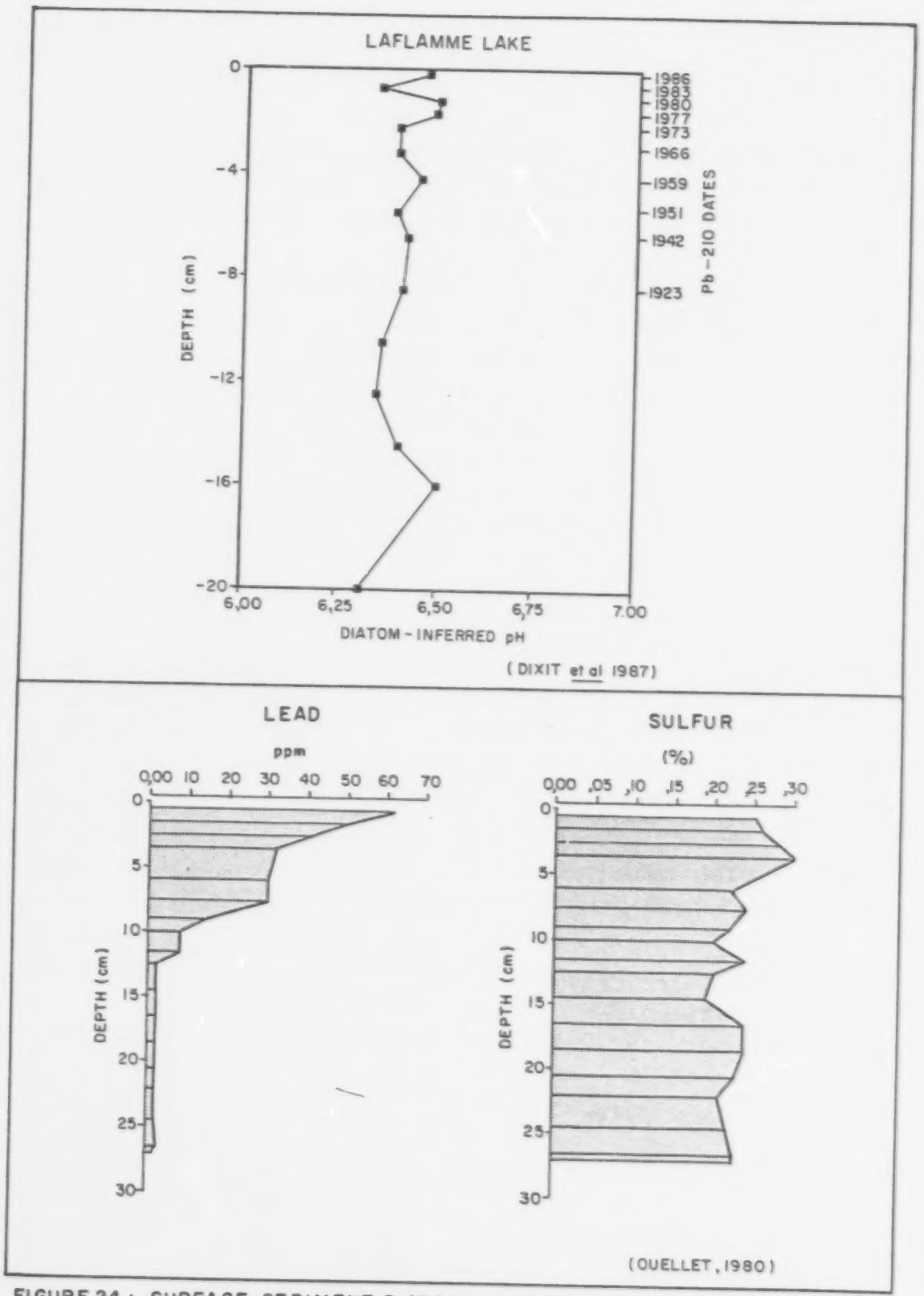

FIGURE 24 : SURFACE SEDIMENT DIATOM-INFERRED pH , LEAD AND SULFUR CONCENTRATION.

6. WATER AND CHEMICAL BUDGETS FOR THE WATERSHED

6.1 Water Budgets

In the simplest of cases, the main input into a headwater system is incoming precipitation and the main outputs are evapotranspiration and streamflow. However inputs will only equal outputs if changes in water storage within the watershed are negligible. As changes in storage, especially the soil compartment are difficult to measure, the selection of an appropriate water year can bypass the problem. By beginning the hydrological year on June 1, the snowpack has completely melted and meltwater has recharged the soil so changes in soil water and snowpack storage need not be considered in the budget. The LLW also differs from the simple case due to the presence of an underground flow system which means not all water leaves via streamflow or evaporation.

Parameters that have been measured for the watershed on a regular basis are precipitation, snow and rain fractions, outflow, changes in lake level and pan evaporation (table 23). Precipitation amounts were discussed earlier. The five year annual average was 1,31 m of which 0,43 m fell as snow.

Outflow represents roughly 61% of incoming precipitation (figure 9). The weekly hydrograph is presented in figure 25. Peak flows in the order of 0,1 m^3/s occur in May. Low flows of 0,002 m^3/s are seen in winter months. Lake evaporation is about 0,17 x 10^5 m^3 or 28 cm. The difference between the highest and lowest lake level recorded is 0,29 m. Both increases and decreases in lake level have been measured from one year to another. On June 1, 1984 and 1985, the lake was at the same level.

Several other hydrological parameters are not measured directly but rather estimated. Interception losses are considered to be similar to values found in 1981 and 1982 (table 9). Snowpack evaporation is estimated at 0,25 x 10^5 m^3. Very little data is available on soil evaporation. This factor is believed to be the cause of the 9% of incoming precipitation that is not accounted for in the budget. If so, evaporation losses would be 32% of incoming precipitation.

Table 23. MONTHLY PRECIPITATION AND OUTFLOW FOR LAFLAMME LAKE WATERSHED

Date		Precipitation APN (mm)	Snow APN (mm)	Precipitation Watershed (mm)	Snow (mm)	Total outflow (mm)	Total outflow ($10^3 m^3$)	average (m^3/sec)	Outflow maximum (m^3/sec)	minimum (m^3/sec)	Evaporation Bac (mm)
January	1981	26.4	26.4	25.6	25.6	15.4	10.5	0.122	0.004	0.005	0.003	0.0
February	1981	235.8	130.0	228.7	126.1	74.0	50.6	0.586	0.021	0.067	0.004	0.0
March	1981	89.1	54.0	86.4	52.4	38.0	26.0	0.301	0.010	0.033	0.006	0.0
April	1981	124.7	23.0	121.0	22.3	146.3	100.1	1.158	0.039	0.092	0.016	0.0
May	1981	124.2	4.0	120.5	3.9	220.6	150.9	1.747	0.056	0.093	0.030	0.0
June	1981	192.4	0.0	186.6	0.0	107.1	73.3	0.848	0.028	0.067	0.013	112.1
July	1981	78.6	0.0	76.2	0.0	74.3	50.8	0.588	0.019	0.071	0.007	138.5
August	1981	190.7	0.0	185.0	0.0	97.9	67.0	0.775	0.025	0.056	0.006	89.5
September	1981	93.6	8.0	90.8	7.8	39.2	26.8	0.310	0.010	0.026	0.004	56.9
October	1981	112.0	20.0	108.6	19.4	52.3	35.8	0.414	0.013	0.032	0.007	0.0
November	1981	47.0	34.0	45.6	33.0	43.1	29.5	0.341	0.011	0.018	0.006	0.0
December	1981	54.8	53.0	53.2	51.4	24.2	16.6	0.192	0.006	0.008	0.005	0.0
Total		1369	352	1328	342	932	638	7.382				397.0

Computer listings are not in metric format.

Table 23. MONTHLY PRECIPITATION AND OUTFLOW FOR LAFLAMME LAKE WATERSHED

Date		Precipitation APN (mm)	Snow APN (mm)	Precipitation Watershed (mm)	Snow (mm)	(mm)	Total outflow ($10^3 m^3$)	(m^3/sec)	average (m^3/sec)	Outflow maximum (m^3/sec)	minimum (m^3/sec)	Evaporation Bac (mm)
June	1981	192.4	0.0	186.6	0.0	107.1	73.3	0.848	0.028	0.067	0.013	112.1
July	1981	78.6	0.0	76.2	0.0	74.3	50.8	0.588	0.019	0.071	0.007	138.5
August	1981	190.7	0.0	185.0	0.0	97.9	67.0	0.775	0.025	0.056	0.006	89.5
September	1981	93.6	8.0	90.8	7.8	39.2	26.8	0.310	0.010	0.026	0.004	56.9
October	1981	112.0	20.0	108.6	19.4	52.3	35.8	0.414	0.013	0.032	0.007	0.0
November	1981	47.0	34.0	45.6	33.0	43.1	29.5	0.341	0.011	0.018	0.006	0.0
December	1981	54.8	53.0	53.2	51.4	24.2	16.6	0.192	0.006	0.008	0.005	0.0
January	1982	111.7	111.7	108.3	108.3	19.2	13.1	0.152	0.005	0.012	0.002	0.0
February	1982	31.5	31.5	30.6	30.6	13.0	8.9	0.103	0.004	0.007	0.002	0.0
March	1982	110.9	85.0	107.6	82.5	14.1	9.7	0.112	0.004	0.007	0.002	0.0
April	1982	95.4	66.0	92.5	64.0	24.4	16.7	0.193	0.006	0.013	0.003	0.0
May	1982	38.8	0.0	37.6	0.0	170.1	116.4	1.347	0.043	0.095	0.012	0.0
Total		1157	409	1123	397	679	464	5.375				397.0

Table 23. MONTHLY PRECIPITATION AND OUTFLOW FOR LAFLAMME LAKE WATERSHED

Date		Precipitation APN (mm)	Snow APN (mm)	Precipitation Watershed (mm)	Snow (mm)	Total outflow (mm)	Total outflow ($10^3 m^3$)	Outflow (m^3/sec)	average (m^3/sec)	Outflow maximum (m^3/sec)	minimum (m^3/sec)	Evaporation Bac (mm)
June	1982	113.3	0.0	109.9	0.0	57.7	39.5	0.457	0.015	0.042	0.005	110.0
July	1982	96.8	0.0	93.9	0.0	38.8	26.5	0.307	0.010	0.022	0.002	126.9
August	1982	119.2	0.0	115.6	0.0	33.7	23.1	0.267	0.009	0.015	0.003	84.0
September	1982	114.4	0.0	111.0	0.0	64.4	44.1	0.510	0.017	0.032	0.009	48.6
October	1982	57.5	5.0	55.8	4.8	36.4	24.9	0.288	0.009	0.016	0.006	0.0
November	1982	194.3	54.5	188.5	52.9	106.5	72.8	0.843	0.028	0.081	0.007	0.0
December	1982	152.8	56.0	148.2	54.3	75.8	51.8	0.600	0.019	0.039	0.009	0.0
January	1983	101.0	63.0	98.0	61.1	49.4	33.8	0.391	0.013	0.042	0.007	0.0
February	1983	125.6	64.0	121.8	62.1	42.1	28.8	0.333	0.012	0.053	0.006	0.0
March	1983	96.7	53.0	93.8	51.4	29.9	20.5	0.237	0.008	0.032	0.004	0.0
April	1983	194.7	87.0	188.9	84.4	77.0	52.7	0.610	0.020	0.079	0.005	0.0
May	1983	242.7	3.2	235.4	3.1	286.8	196.2	2.271	0.073	0.102	0.035	0.0
Total		1609	386	1561	374	898	615	7.114				369.5

Table 23. MONTHLY PRECIPITATION AND OUTFLOW FOR LAFLAMME LAKE WATERSHED

Date		Precipitation APN (mm)	Snow APN (mm)	Precipitation Watershed (mm)	Snow (mm)	(mm)	Total outflow ($10^3 m^3$)	(m^3/sec)	average (m^3/sec)	Outflow maximum (m^3/sec)	minimum (m^3/sec)	Evaporation Bac (mm)
June	1983	75.1	0.2	72.8	0.2	115.1	78.7	0.911	0.030	0.080	0.010	151.7
July	1983	139.4	0.0	135.2	0.0	59.6	40.8	0.472	0.015	0.046	0.006	138.2
August	1983	68.1	0.0	66.1	0.0	38.9	26.6	0.308	0.010	0.041	0.004	113.5
September	1983	174.6	0.0	169.4	0.0	62.9	43.0	0.498	0.017	0.037	0.005	75.5
October	1983	109.8	6.9	106.5	6.7	65.4	44.8	0.518	0.017	0.030	0.010	0.0
November	1983	164.9	112.1	160.0	108.7	38.4	26.3	0.304	0.010	0.020	0.002	0.0
December	1983	179.6	173.3	174.2	168.1	34.4	23.5	0.272	0.009	0.014	0.005	0.0
January	1984	47.6	46.6	46.2	45.2	19.5	13.3	0.154	0.005	0.006	0.004	0.0
February	1984	95.4	75.5	92.5	73.2	17.8	12.2	0.141	0.005	0.010	0.002	0.0
March	1984	60.0	39.8	58.2	38.6	18.7	12.8	0.148	0.005	0.012	0.002	0.0
April	1984	75.1	21.9	72.8	21.2	66.8	45.7	0.529	0.018	0.083	0.002	0.0
May	1984	148.7	23.3	144.2	22.6	253.0	173.1	2.003	0.065	0.099	0.031	0.0
Total		1338	500	1298	485	790	541	6.258				478.9

Table 23. MONTHLY PRECIPITATION AND OUTFLOW FOR LAFLAMME LAKE WATERSHED

Date		Precipitation APN (mm)	Snow APN (mm)	Precipitation Watershed (mm)	Snow (mm)	(mm)	Total outflow ($10^3 m^3$)	(m^3/sec)	average (m^3/sec)	Outflow maximum (m^3/sec)	minimum (m^3/sec)	Evaporation Bac (mm)
June	1984	91.4	0.0	88.7	0.0	83.1	56.9	0.658	0.022	0.038	0.010	118.0
July	1984	148.0	0.0	143.6	0.0	74.4	50.9	0.589	0.019	0.069	0.007	114.0
August	1984	99.0	0.0	96.0	0.0	35.4	24.2	0.280	0.009	0.022	0.004	108.0
September	1984	104.2	0.8	101.1	0.8	35.0	23.9	0.277	0.009	0.025	0.004	59.0
October	1984	51.4	8.7	49.9	8.4	34.1	23.3	0.270	0.009	0.012	0.006	0.0
November	1984	126.2	34.7	122.4	33.7	55.8	38.2	0.442	0.015	0.037	0.008	0.0
December	1984	117.5	99.4	114.0	96.4	42.6	29.1	0.337	0.011	0.015	0.008	0.0
January	1985	56.6	56.6	54.9	54.9	19.8	13.6	0.157	0.005	0.013	0.000	0.0
February	1985	104.5	104.5	101.4	101.4	16.9	11.6	0.134	0.005	0.008	0.003	0.0
March	1985	93.2	89.2	90.4	86.5	16.0	11.0	0.127	0.004	0.008	0.002	0.0
April	1985	111.4	36.0	108.1	34.9	49.0	33.5	0.388	0.013	0.053	0.003	0.0
May	1985	146.5	8.5	142.1	8.2	241.1	164.9	1.909	0.062	0.098	0.025	40.4
Total		1250	438	1212	425	703	481	5.568				439.4

Table 23. MONTHLY PRECIPITATION AND OUTFLOW FOR LAFLAMME LAKE WATERSHED

Date		Precipitation APN (mm)	Snow APN (mm)	Precipitation Watershed (mm)	Snow (mm)	(mm)	Total outflow ($10^3 m^3$)	(m^3/sec)	average (m^3/sec)	Outflow maximum (m^3/sec)	minimum (m^3/sec)	Evaporation Bac (mm)
June	1985	123.5	0.0	119.8	0.0	116.2	79.5	0.920	0.031	0.068	0.015	84.8
July	1985	197.0	0.0	191.1	0.0	99.1	67.8	0.785	0.025	0.061	0.012	124.1
August	1985	49.2	0.0	47.7	0.0	35.5	24.3	0.281	0.009	0.017	0.005	98.6
September	1985	119.1	0.0	115.5	0.0	29.8	20.4	0.236	0.008	0.034	0.003	65.5
October	1985	120.5	7.3	116.9	7.1	67.1	45.9	0.531	0.017	0.045	0.009	8.0
November	1985	89.6	41.9	86.9	40.6	48.9	33.4	0.387	0.013	0.025	0.008	0.0
December	1985	112.4	71.6	109.0	69.5	45.8	31.4	0.363	0.012	0.029	0.006	0.0
January	1986	176.3	152.1	171.0	147.5	36.5	25.0	0.289	0.009	0.037	0.003	0.0
February	1986	20.7	20.7	20.1	20.1	16.0	11.0	0.127	0.005	0.008	0.003	0.0
March	1986	106.8	101.4	103.6	98.4	20.7	14.2	0.164	0.005	0.009	0.003	0.0
April	1986	105.9	90.1	102.7	87.4	153.6	105.1	1.216	0.041	0.193	0.009	0.0
May	1986	160.1	14.9	155.3	14.5	223.9	153.2	1.773	0.057	0.198	0.018	0.0
Total		1381	500	1340	485	893	611	7.072				381.0

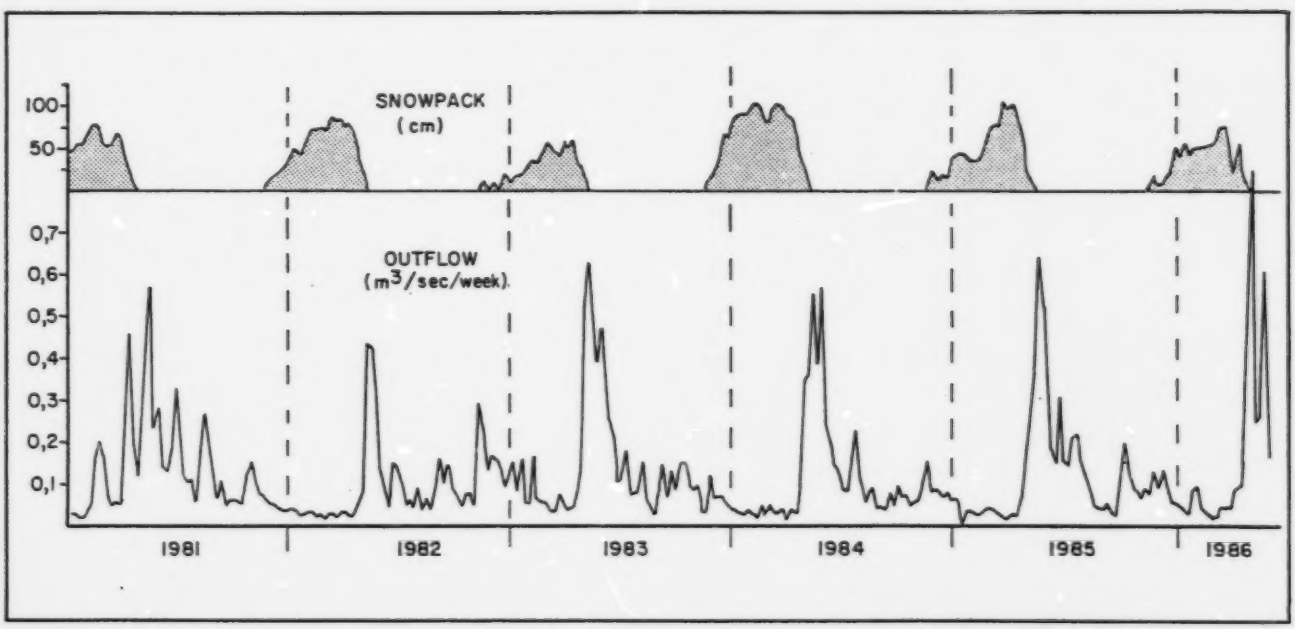

FIGURE 25 : OUTFLOW AND SNOWPACK ACCUMULATION IN LAFLAMME LAKE WATERSHED.

Groundwater losses from the watershed were calculated by Robitaille et al. (1983a). Half of the underground valley had a higher permeability (2×10^{-5} m/s) than the other half (9×10^{-7} m/s). The outflow was calculated to be 54,2 m^3/day or under maximum conditions 126,4 m^3/day (5% of incident precipitation). Deschenes and Villeneuve (1983) applied a coupled surface and groundwater hydrological model to the watershed data and found that 7% of incident precipitation flowed in the underground valley below the lake. Groundwater losses are considered to be about 7% in the water budget.

The most difficult estimations of water pathways occurs in the recharge area, where water is partitionned between runoff, shallow flow, streamflow and groundwater flow.

Many factors indicate the qualitative importance of groundwater recharge in the system. The nature of the local topography, the nature and permeability of surficial deposits as well as the almost inexistant surface drainage network all tend to indicate that the recharge of the lake is mainly by groundwater (Azzaria et al., 1982). Most soils in humid regions such as LLW have a large infiltration capacity due mainly to the abundant humus layer which means that surface runoff will be practically inexistant in periods without frost. As long as the watertable is below the soil surface, all water that falls on the soil can infiltrate. The outflow hydrograph shows rapid increases but slower declines; this is also an indication that precipitation percolates into deeper soil horizons. Lastly, lake quality is similar to groundwater quality during most of the year except during high flow periods. Unless very important in-lake processes occur such as neutralization by the sediments, water chemistry would not be consistant with recharge from acidic sources such as runoff, precipitation and shallow interflow.

Outflow data indicates that about 60% of total discharge occurs under these conditions. However the remaining part of annual flow occurs in April and May when it is difficult to see how water is flowing in the system. The magnitude of changes in surface water quality indicates that water is probably being rerouted along pathways with rapid or no contact with acid neutralizing components. There has been no study that clearly quantifies the pathways in the spring. On the first hand, the model used by Deschenes and Villeneuve

predicts a large annual surface flow (55% surface flow to 22% infiltration) which requires a large spring surface flow. On the other hand, Padilla et al. (1983) with a hydrograph separation technique found that the groundwater contribution to recharge was not less than 67% during the spring melt of 1983. During the high flow period in early May, 74% of recharge was groundwater while 26% was runoff.

With all the above considerations taken into account, the water balance for the 1983-1984 year is given in figure 26.

6.2 Mass Balance for the Watershed

Inputs into a headwater system are basically limited to atmospheric deposition (wet, dry and fog). In LLW, wet deposition is obtained by summing the product of daily amount of precipitation by the concentration of each species for that day. A monthly adjustment is carried out for precipitation which has not been analyzed during the month.

Output of material can occur by streamflow and by the groundwater system. Stream output is the sum of the product of weekly flow by average weekly concentration. For the period before sampling started at the stream, lake chemistry data is used in calculations.

As mentioned earlier (table 7), atmospheric wet loading averaged 22 kg/ha sulphate (22,8 mmol/m^2), 0,48 kg/ha hydrogen ion (48 mmol/m^2) and 3,28 kgN/ha nitrate (23,4 mmol/m^2). Periods of high sulphate loading include May to August 1981 (10,1 kg/ha), March and April 1982 (4,6 kg/ha), November and December 1982 (6,0 kg/ha), May to July 1983 (10,5 kg/ha), May to July 1984 (10,2 kg/ha) (tables 24-27). This indicates that almost half of the annual loading is received during three to four months. In July 1984, over 5 kg/ha of sulphate were received during the month. Low atmospheric loading (less than 1 kg/ha/month) is usually received during winter months. The hydrogen ion loading follows the same pattern as sulphate loading although the former is influenced by high nitrate deposition in some winter months. The pattern of nitrate loading is the most different of the three parameters.

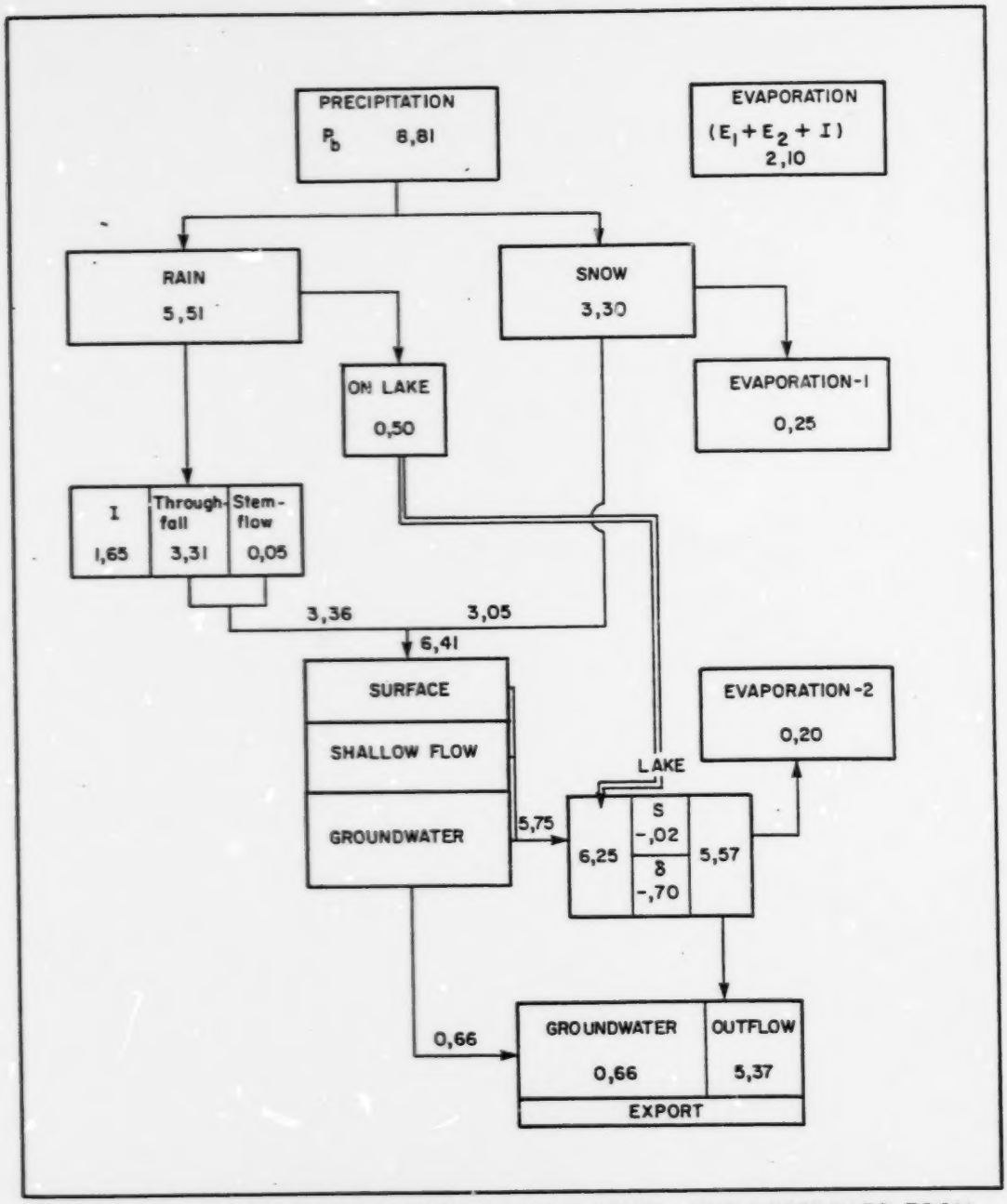

FIGURE 26 : WATER BUDGET FOR THE LAFLAMME LAKE WATERSHED FROM JUNE 1983 TO MAY 1984 (VOLUME IN $10^5 m^3$).

Table 24. Monthly wet loading and stream chemical output in 1981 (kg/ha)

Month	H+	Ca++	Mg++	Na+	K+	N NH4+	SO4--	Cl-	N NO3-	Precipitation cm
January	0.009	0.05	0.006	0.02	0.010	0.14	0.50	0.10	0.18	26.4
I	2	3	3	2	3	7	2	8	6	1
February	0.043	0.14	0.030	0.35	0.034	0.12	1.50	0.25	0.42	235.0
I	11	11	15	29	12	6	7	22	14	17
March	0.020	0.06	0.010	0.15	0.019	0.17	1.20	0.14	0.26	89.1
I	5	4	5	12	6	9	6	12	8	6
April	0.028	0.30	0.037	0.09	0.027	0.23	1.78	0.07	0.40	124.7
I	7	23	19	7	10	13	9	6	13	9
May	0.046	0.15	0.027	0.16	0.036	0.21	2.80	0.11	0.26	124.2
I	12	12	14	12	13	12	14	9	8	9
June	0.052	0.13	0.018	0.05	0.040	0.25	2.81	0.07	0.27	192.4
I	13	10	9	4	14	14	14	6	9	14
July	0.030	0.08	0.007	0.07	0.012	0.13	1.60	0.03	0.14	78.6
I	8	6	3	5	4	7	8	2	4	5
August	0.050	0.11	0.018	0.10	0.030	0.20	2.90	0.06	0.24	190.7
I	13	8	9	8	11	11	14	5	8	13
September	0.029	0.03	0.007	0.03	0.015	0.13	1.47	0.07	0.14	93.6
I	7	2	3	2	5	7	7	6	4	6
October	0.040	0.12	0.017	0.04	0.017	0.16	1.91	0.12	0.34	112.0
I	10	9	8	3	6	9	9	10	11	8
November	0.015	0.03	0.006	0.05	0.019	0.01	0.51	0.03	0.10	47.0
I	3	2	3	4	7	0	2	2	3	3
December (e)	0.013	0.05	0.006	0.09	0.010	0.01	0.32	0.08	0.17	54.8
I	3	3	3	7	3	0	1	7	5	4
total	0.376	1.25	0.190	1.22	0.269	1.77	19.39	1.12	2.91	1369.3

(e) estimated

Month	H+	Ca++	Mg++	Na+	K+	Alk	SO4--	Cl-	N NO3-	Al	Pt
January *	0.00030	0.46	0.09	0.18	0.03	0.95	0.63	0.15	0.03	0.01	0.008
I	1.5	2	2	3	2	3	1	5	2	1	2
February*	0.00320	1.93	0.38	0.62	0.14	2.82	3.17	0.42	0.25	0.09	0.028
I	16.3	10	10	9	9	10	7	14	16	8	7
March *	0.00170	0.99	0.18	0.32	0.07	1.00	2.77	0.12	0.16	0.05	0.015
I	8.7	5	5	5	5	3	6	4	10	5	4
April	0.01000 *	3.05	0.51	0.80	0.33	1.56	8.15	0.39	0.50	0.16	0.097
I	51.1	16	13	13	21	5	17	13	32	15	24
May	0.00246	4.00	0.85	1.20	0.39	7.20	13.20	0.59	0.40	0.32	0.077
I	12.6	21	22	10	26	25	20	20	30	30	19
June	0.00057	1.95	0.44	0.70	0.14	2.58	6.52	0.28	0.05	0.11	0.046
I	2.9	10	11	10	9	9	14	10	3	10	11
July	0.00035	1.26	0.31	0.51	0.09	1.69	3.65	0.20	0.02	0.10	0.031
I	1.8	6	8	7	6	6	8	7	1	9	8
August	0.00039	2.00	0.43	0.85	0.14	2.85	3.78	0.30	0.03	0.11	0.035
I	2.0	11	11	12	9	10	8	10	2	10	9
September	0.00018	0.87	0.18	0.38	0.05	1.58	1.39	0.09	0.00	0.03	0.015
I	0.9	4	5	5	3	6	3	3	0	3	4
October	0.00017	1.27	0.25	0.53	0.03	2.71	1.69	0.16	0.01	0.03	0.022
I	0.9	6	6	8	2	9	4	5	1	3	6
November	0.00015	1.02	0.21	0.44	0.07	2.22	1.57	0.17	0.03	0.03	0.017
I	0.8	5	5	6	5	8	3	6	2	3	4
December	0.00011	0.61	0.12	0.25	0.04	1.60	0.88	0.10	0.03	0.02	0.011
I	0.6	3	3	4	3	6	2	3	2	2	3
total	0.01957	19.57	3.93	6.94	1.53	28.75	47.39	2.98	1.59	1.067	0.403

* estimated from lake values

Table 25. Monthly wet loading and stream chemical output in 1982 (kg/ha)

Month	H+	Ca++	Mg++	Na+	K+	N NH4+	SO4--	Cl-	N NO3-	Precipitation mm
January (a)	0.025	0.12	0.012	0.20	0.010	0.03	0.42	0.19	0.39	111.7
I	4	12	9	19	4	1	1	8	11	9
February	0.007	0.01	0.002	0.06	0.002	0.01	0.38	0.16	0.11	31.5
I	1	0	1	5	0	0	1	7	3	2
March	0.066	0.10	0.013	0.12	0.020	0.15	2.05	0.33	0.42	110.9
I	13	10	10	11	9	8	9	15	12	8
April	0.063	0.10	0.017	0.08	0.015	0.16	2.54	0.32	0.28	95.4
I	12	10	13	7	6	9	12	15	8	7
May	0.036	0.00	0.003	0.05	0.008	0.14	1.37	0.06	0.13	38.8
I	7	0	2	4	3	8	6	2	3	3
June	0.041	0.07	0.009	0.08	0.038	0.28	2.36	0.22	0.26	113.3
I	8	7	6	7	17	15	11	10	7	9
July	0.025	0.10	0.010	0.06	0.015	0.13	1.43	0.17	0.14	96.8
I	4	10	8	5	6	7	6	7	4	7
August	0.033	0.12	0.013	0.10	0.023	0.17	1.78	0.11	0.22	119.2
I	6	12	10	9	10	9	8	5	6	9
September	0.033	0.06	0.010	0.05	0.016	0.14	1.71	0.12	0.15	114.4
I	6	6	7	4	7	8	8	5	4	9
October	0.026	0.03	0.006	0.03	0.013	0.12	1.18	0.07	0.16	57.5
I	5	2	4	3	5	6	5	3	4	4
November	0.083	0.08	0.017	0.09	0.036	0.25	3.01	0.17	0.68	194.3
I	16	9	15	8	15	14	14	8	20	15
December	0.065	0.08	0.014	0.15	0.028	0.15	2.90	0.19	0.42	152.8
I	12	8	10	13	12	8	13	9	12	12
Total	0.504	0.93	0.127	1.07	0.222	1.74	21.14	2.11	3.36	1256.6

Month	H+	Ca++	Mg++	Na+	K+	Alk	SO4--	Cl-	N NO3-	Al	Pi
January	0.00007	0.53	0.11	0.21	0.03	1.44	0.66	0.07	0.03	0.01	0.009
I	0.8	4	4	4	2	5	3	2	3	1	4
February	0.00005	0.38	0.08	0.15	0.03	1.14	0.46	0.06	0.02	0.01	0.005
I	0.5	3	3	3	2	4	2	2	2	1	2
March	0.00012	0.43	0.09	0.17	0.04	0.99	0.50	0.06	0.03	0.01	0.006
I	1.2	3	3	3	2	3	2	2	3	1	3
April	0.00024	0.74	0.14	0.29	0.06	2.00	0.91	0.09	0.07	0.02	0.012
I	2.5	5	5	5	4	7	4	3	6	2	5
May	0.00401	3.87	0.58	1.03	0.62	4.64	6.11	0.63	0.57	0.30	0.074
I	68.7	26	20	19	43	16	24	21	51	30	31
June	0.00031	1.32	0.25	0.49	0.16	2.39	2.22	0.41	0.04	0.10	0.017
I	3.1	9	8	9	11	8	9	14	4	10	7
July	0.00020	0.79	0.18	0.36	0.07	1.80	1.58	0.25	0.01	0.06	0.012
I	2.0	5	6	6	5	6	6	8	1	6	5
August	0.00015	0.70	0.18	0.28	0.06	1.94	1.18	0.15	0.00	0.04	0.009
I	1.6	5	6	5	4	7	5	5	0	4	4
September	0.00049	1.42	0.31	0.63	0.13	3.78	2.27	0.26	0.01	0.09	0.022
I	4.9	9	11	11	9	13	9	9	1	9	9
October	0.00015	0.86	0.17	0.35	0.06	2.46	1.27	0.14	0.01	0.04	0.013
I	1.5	6	6	6	4	8	5	5	1	4	6
November	0.00068	2.27	0.49	0.90	0.11	4.73	4.61	0.50	0.13	0.18	0.038
I	6.9	15	17	16	7	16	18	17	12	17	16
December	0.00062	1.60	0.33	0.67	0.10	2.35	3.64	0.35	0.18	0.14	0.021
I	6.2	11	11	12	7	8	14	12	16	14	9
Total	0.00990	14.92	2.91	5.52	1.45	29.65	25.43	2.97	1.10	1.017	0.240

(a) estimated from less than 50% of volume analyzed

Table 26. Monthly wet loading and stream chemical output in 1983 (kg/ha)

Month	H+	Ca++	Mg++	Na+	K+	N NH_4^+	SO_4^{--}	Cl^-	N NO_3^-	Precipitation mm
January	0.020	0.04	0.007	0.04	0.013	0.04	0.47	0.12	0.17	101.0
I	3	1	2	5	3	1	1	4	5	6
February	0.031	0.05	0.009	0.05	0.026	0.05	0.81	0.21	0.27	125.6
I	5	2	3	6	6	2	3	7	8	7
March	0.011	0.03	0.007	0.02	0.013	0.01	0.53	0.09	0.05	96.7
I	2	1	2	2	3	0	2	3	1	5
April	0.042	0.08	0.020	0.13	0.026	0.11	1.93	0.24	0.20	194.7
I	8	4	7	16	7	4	8	8	6	11
May	0.113	0.21	0.028	0.08	0.053	0.38	4.50	0.14	0.55	242.7
I	21	11	11	10	13	15	18	4	17	14
June	0.055	0.05	0.008	0.04	0.025	0.27	2.58	0.08	0.21	75.1
I	10	2	2	4	6	10	10	2	6	4
July	0.060	0.18	0.026	0.14 e	0.059	0.40	3.37	0.30	0.27	139.4
I	11	9	10	18	15	16	14	10	8	8
August	0.023	0.14	0.020	0.00	0.011	0.16	1.28	0.28	0.13	68.1
I	4	7	7	0	2	6	5	9	3	4
September	0.063	0.26	0.043	0.00	0.056	0.52	3.89	0.47 e	0.33	174.6
I	12	13	17	0	14	21	16	16	10	10
October	0.027 e	0.22	0.036	0.26 e	0.046	0.24	1.80 e	0.20 e	0.20	109.8
I	5	11	14	34	11	9	7	9	8	6
November	0.047	0.50	0.034	0.00	0.029	0.26	2.07	0.72 e	0.42	164.9
I	8	26	13	0	7	10	8	24	13	9
December	0.026	0.14	0.018	0.00	0.027	0.00	0.64	0.00	0.29	179.6
I	5	7	6	0	6	0	2	0	9	10
Total	0.518	1.91	0.256	0.77 p	0.38e	2.44p	23.9e	2.94p	3.17	1672.2

Month	H+	Ca++	Mg++	Na+	K+	Alk	SO_4^{--}	Cl^-	N NO_3^-	Al	Pt
January	0.00039	1.22	0.24	0.66	0.08	1.85	2.44	0.20	0.13	0.07	0.011
I	2.1	7	7	8	2	6	7	5	13	9	5
February	0.00024	1.15	0.22	0.41	0.09	1.94	1.93	0.17	0.12	0.05	0.011
I	1.3	7	7	7	2	6	5	5	12	6	5
March	0.00012	0.93	0.18	0.34	0.07	2.04	1.30	0.16	0.09	0.03	0.009
I	0.6	6	5	6	2	7	4	4	9	4	4
April	0.00270	1.47	0.28	0.50	0.45	2.08	2.92	0.34	0.19	0.07	0.029
I	14.8	9	8	8	12	9	8	9	19	9	12
May	0.01334	3.66	0.57	1.15	1.03	5.07	10.14	1.25	0.34	0.26	0.086
I	70.8	22	17	19	49	16	29	33	34	35	36
June	0.00062	1.96	0.39	0.74	0.48	3.66	4.36	0.64	0.05	0.09	0.024
I	3.3	12	12	12	13	12	12	17	5	12	10
July	0.00018	1.02	0.27	0.38	0.24	2.05	2.54	0.27	0.01	0.04	0.014
I	0.9	6	8	6	6	7	7	7	1	5	6
August	0.00011	0.69	0.17	0.30	0.08	1.53	1.56	0.14	0.00	0.03	0.008
I	0.6	4	5	5	2	5	4	4	0	4	3
September	0.00028	1.28	0.29	0.52	0.13	2.09	2.51	0.16	0.01	0.04	0.014
I	1.5	8	9	9	3	9	7	4	1	5	6
October	0.00043	1.48	0.33	0.53	0.13	3.14	2.58	0.21	0.01	0.04	0.015
I	2.3	9	10	9	4	10	7	5	1	5	6
November	0.00025	0.90	0.20	0.35	0.09	2.06	1.48	0.16	0.02	0.02	0.011
I	1.3	5	6	6	2	7	4	4	2	3	4
December	0.00011	0.87	0.19	0.33	0.07	2.33	1.41	0.14	0.03	0.02	0.006
I	0.6	5	6	6	2	7	4	4	3	3	2
Total	0.01884	16.64	3.33	6.03	3.72	31.13	35.17	3.83	1.01	0.738	0.237

p: partial
e: estimated when volume analysed is less than 50%
0.00: volume analysed less than 20%

Table 27. Monthly wet loading and stream chemical output in 1984 (kg/ha)

Month	H+	Ca++	Mg++	Na+	K+	N NH4+	SO4--	Cl-	N NO3-	Precipitation mm
January	0.042	0.02	0.004	0.00	0.015	0.15	1.18	0.17 e	0.39	47.6
I	8	1	1	0	5	6	5	8	10	4
February	0.032	0.07	0.013	0.00	0.015	0.11 e	1.01	0.27 e	0.30	95.6
I	6	4	4	0	4	5	4	13	8	8
March	0.022	0.16	0.023	0.00	0.016	0.08	1.02	0.15 e	0.25	60.0
I	4	10	8	9	5	3	4	7	6	5
April	0.003	0.27	0.059	0.45	0.029	0.24 e	0.78	0.38	0.07	75.1
I	0	17	22	63	9	10	3	19	1	6
May	0.070	0.42	0.054	0.00	0.053	0.36	3.60	0.42 e	0.38	148.7
I	13	27	20	0	17	16	15	21	10	12
June	0.028	0.00	0.014	0.00	0.034	0.13	1.47	0.00	0.15	91.4
I	5	0	5	0	11	5	6	0	4	7
July	0.092	0.45	0.037	0.00	0.042	0.33	5.10	0.40 e	0.42	148.0
I	18	28	13	9	14	14	21	19	11	12
August	0.042	0.00	0.014	0.00	0.034	0.27	2.31	0.00	0.20	99.0
I	8	0	5	0	11	11	9	0	5	8
September	0.051	0.00	0.010	0.00	0.022	0.27	2.68	0.00	0.27	104.2
I	10	0	3	0	7	11	11	0	7	8
October	0.024	0.03	0.007	0.20	0.011	0.08	1.18	0.11 e	0.13	51.4
I	4	2	2	20	3	3	5	5	3	4
November	0.057	0.08	0.020	0.00	0.018	0.19	2.15	0.00	0.49	126.2
I	11	4	7	0	6	8	9	0	13	10
December	0.046	0.06	0.009	0.06	0.011	0.06	0.75	0.09	0.61	117.5
I	8	3	3	8	3	2	3	4	16	10
total	0.518	1.55 p	0.265	0.71 p	0.302	2.27	23.23	1.99 p	3.66	1164.5

Month	H+	Ca++	Mg++	Na+	K+	Alk	SO4--	Cl-	N NO3-	Al	Pt
January	0.00008	0.52	0.11	0.20	0.04	1.28	0.74	0.08	0.02	0.01	0.005
I	0.8	3	3	3	4	5	2	3	3	2	2
February	0.00006	0.50	0.11	0.19	0.04	1.31	0.69	0.07	0.03	0.01	0.005
I	0.7	4	4	3	4	5	2	3	3	1	2
March	0.00009	0.54	0.11	0.20	0.06	1.45	0.72	0.08	0.04	0.01	0.007
I	1.0	4	4	4	5	6	2	3	5	2	3
April	0.00170	1.38	0.28	0.52	0.15	2.22	2.77	0.25	0.26	0.05	0.015
I	19.6	10	9	10	14	9	9	9	30	8	7
May	0.00527	4.14	0.87	1.51	0.40	4.44	11.53	0.97	0.42	0.26	0.052
I	60.2	29	28	27	36	18	36	35	49	43	25
June	0.00033	1.49	0.32	0.51	0.08	2.34	3.66	0.32	0.02	0.05	0.017
I	3.8	11	10	9	8	10	11	12	2	8	8
July	0.00035	1.29	0.29	0.54	0.07	2.13	3.15	0.24	0.00	0.05	0.018
I	4.1	9	10	10	7	9	10	9	1	8	9
August	0.00009	0.65	0.14	0.27	0.04	1.20	1.55	0.12	0.00	0.03	0.010
I	1.0	5	5	5	3	5	5	4	0	5	5
September	0.00007	0.75	0.17	0.29	0.04	1.61	1.43	0.11	0.00	0.03	0.033
I	0.8	5	6	5	3	7	5	4	0	4	16
October	0.00015	0.73	0.17	0.30	0.04	1.74	1.35	0.12	0.00	0.03	0.017
I	1.7	5	6	6	4	7	4	5	0	5	8
November	0.00021	1.20	0.26	0.50	0.07	2.88	2.37	0.22	0.03	0.04	0.015
I	2.4	8	9	9	6	12	7	8	3	7	7
December	0.00034	1.09	0.23	0.43	0.07	1.89	2.20	0.17	0.04	0.04	0.015
I	3.9	8	7	8	7	8	7	6	5	7	7
total	0.00868	14.19	3.05	5.43	1.08	24.41	31.94	2.72	0.84	0.402	0.200

p: partial
e: estimated when volume analysed is less than 50%
0.00: volume analysed less than 20%

Periods of high loading (1,1 kg N/ha) occurred in November and December 1982 and 1984. Loading was also high in May 1983 and in the fall and early winter of the same year.

The monthly atmospheric inputs of ammonium ion have roughly the same relative importance with respect to total yearly input as sulphate ions with the exception of major differences in December 1982 and 1983 as well as April and July 1984. The inputs of chloride and calcium ions seem to be rather higher when moving from APN data to CAPMoN data in July of 1983. This is probably related to the use of a new validation process for precipitation data. For parameters present in higher concentration, no shift seems to occur.

The mass of substance exported from the watershed (tables 24-29) is four times higher than atmospheric wet loading. Calcium, sulphate and bicarbonates contribute 83% of the exported mass. Output of ions basically reflects outflow patterns except for nitrate ions. Highest outputs of all parameters occurs in May. Low export occurs in winter months.

Export of hydrogen ions in the spring (April, May) represents 63% in 1981, 71% in 1982, 86% in 1983, 80% in 1984 and 76% in 1985 of total annual output. The highest monthly loading was measured in May 1983 (0,0133 kg/ha). Spring export of nitrate ions is 67% of annual export, while sulphate export and outflow represent 38% of annual totals.

On an annual basis, hydrogen and nitrate ions are retained in the watershed while weathering elements such as Ca, Mg, Na and K are lost from the system (table 30).

In the case of weathering elements, output largely exceeds input all during the year (figure 27). The contribution of atmospheric input to output ranges from 6% for Mg to 10% for Ca to 16% for K and 25% for Na.

Hydrogen ions show the opposite pattern, with atmospheric input always being much greater than output (figure 28). Nitrate, chloride and sulphate ions have crossover patterns (figures 29, 30). Although atmospheric

Table 28. MONTHLY STREAM CHEMICAL OUTPUT IN 1985
(Kg/ha)

Month	H+	Ca++	Mg++	Na+	K+	Alk	SO4--	Cl-	N NO3-	Al	Pt
January	0.00012	0.59	0.13	0.24	0.04	1.36	0.99	0.08	0.03	0.03	0.010
%	1.3	4	4	4	2	5	3	3	3	3	4
February	0.00009	0.61	0.13	0.22	0.05	1.64	0.87	0.08	0.02	0.02	0.009
%	1.0	4	4	4	3	6	3	3	3	2	4
March	0.00011	0.52	0.11	0.19	0.04	1.35	0.69	0.06	0.03	0.01	0.008
%	1.2	3	3	3	2	5	2	2	4	1	3
April	0.00101	1.18	0.25	0.44	0.15	2.47	2.27	0.20	0.18	0.05	0.019
%	11.2	7	7	7	8	9	6	7	22	4	7
May	0.00589	4.06	0.76	1.43	0.75	5.57	10.76	0.93	0.48	0.33	0.074
%	65.2	25	23	24	40	20	30	31	59	31	28
June	0.00058	2.13	0.44	0.72	0.25	2.73	5.31	0.43	0.03	0.15	0.029
%	6.5	13	13	12	14	10	15	15	3	15	11
July	0.00036	1.78	0.37	0.66	0.16	2.79	4.69	0.34	0.01	0.16	0.027
%	4.0	11	11	11	9	10	13	12	1	15	10
August	0.00012	0.67	0.14	0.26	0.04	1.07	1.74	0.11	0.00	0.04	0.010
%	1.4	4	4	4	2	4	5	4	0	4	4
September	0.00010	0.64	0.15	0.25	0.05	1.31	1.34	0.09	0.00	0.03	0.009
%	1.1	4	4	4	3	5	4	3	0	2	3
October	0.00024	1.47	0.34	0.56	0.13	2.79	2.94	0.25	0.00	0.13	0.022
%	2.6	9	10	9	7	10	8	8	0	12	8
November	0.00017	1.19	0.25	0.43	0.10	2.33	2.25	0.20	0.02	0.05	0.021
%	1.9	7	7	7	5	8	6	7	2	4	8
December	0.00023	1.26	0.29	0.48	0.09	2.85	2.48	0.20	0.03	0.05	0.027
%	2.6	8	8	8	5	10	7	7	4	5	10
Total	0.00903	16.14	3.36	5.90	1.87	28.37	36.44	2.98	0.82	1.066	0.265

Table 29. Output of ions at the Laflamme Outlet (kg/ha)

PARAMETER	1984-1985	1985-1986
SO_4	31,29	38,02
Alk	26,25	28,61
Ca	14,16	17,60
Na	5,37	6,03
Mg	2,97	3,65
Cl	2,64	3,36
K	1,44	2,27
Fe	0,87	0,89
$N\text{-}NO_3$	0,83	0,55
Al	0,71	1,29
P	0,24	0,31
Mn	0,17	0,21
Zn	0,03	0,04
H	0,009	0,007

Table 30. Ion Budget for the Laflamme Lake Watershed (kg/ha).

PARAMETER	1981-82			1982-83			1983-84			MEAN
	IN	OUT	NET	IN	OUT	NET	IN	OUT	NET	
H	0,43	0,01	+0,42	0,52	0,02	+0,49	0,47	0,01	+0,46	+0,5
$N-NO_3$	2,73	0,89	+1,84	3,27	1,25	+2,02	3,32	0,90	+2,42	+2,1
Ca	1,0	15,0	-14,0	1,0	17,4	-16,4	2,4	15,3	-12,9	-14,4
Mg	0,1	2,9	- 2,8	0,1	3,4	- 3,3	0,3	3,3	- 3,0	- 3,0
Na	0,9	5,5	- 4,6	0,9	6,5	- 5,6	--	5,8	--	- 5,1
K	0,2	1,3	- 1,1	0,3	3,2	- 2,9	0,4	1,9	- 1,5	- 1,8
SO_4	18,3	28,1	- 9,8	22,6	35,5	-12,9	23,3	32,9	- 9,6	-10,8
Cl	1,5	2,2	-0,7	1,9	4,2	- 2,3	--	3,2	--	- 1,5
Alk	--	25,4	--	--	33,2	--	--	28,1	--	--
Water(cm)	112	68		156	89		130	79		

IN : Atmospheric wet loading
OUT : Stream export
NET : IN - OUT

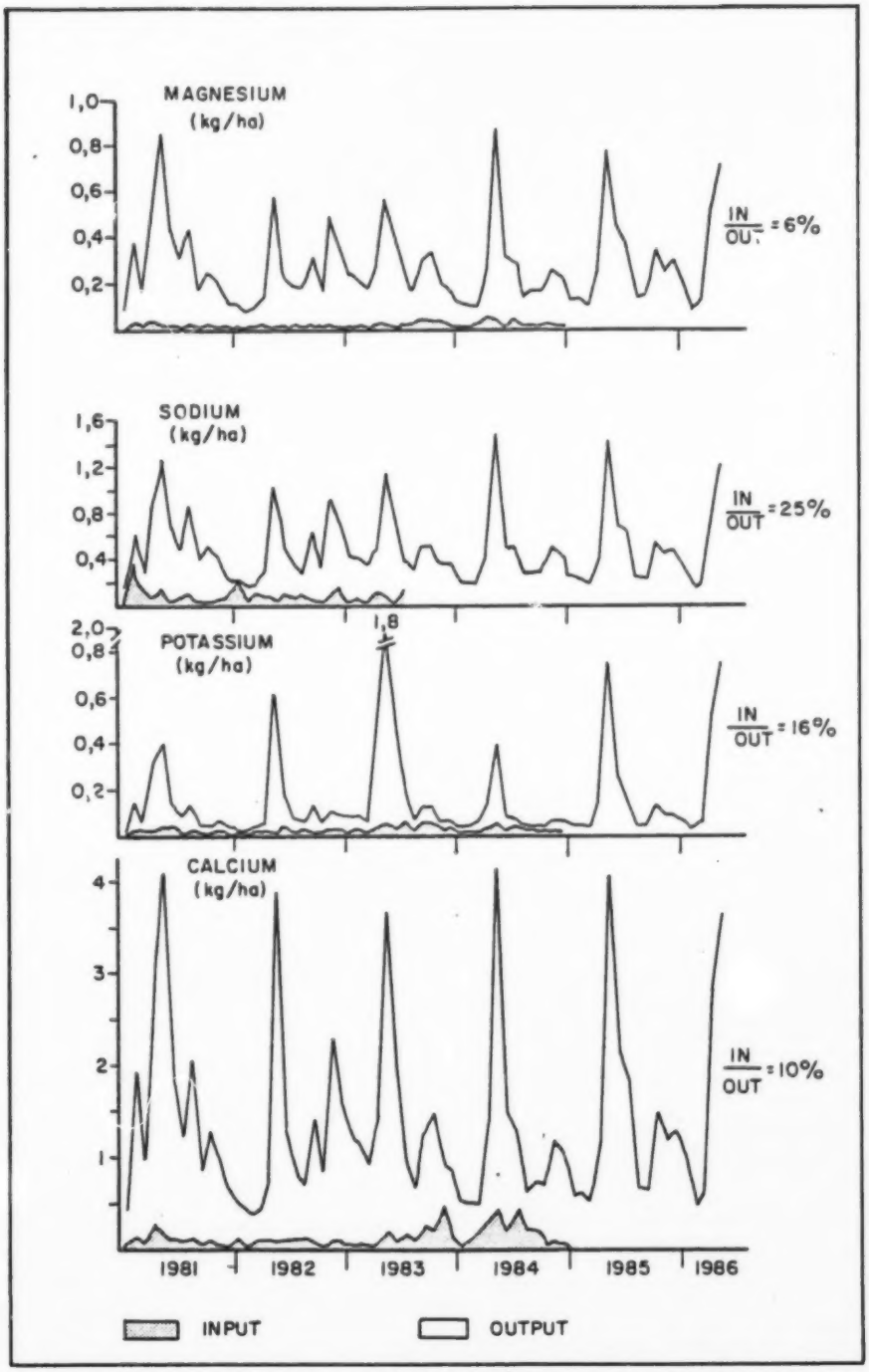

FIGURE 27: MONTHLY FLUX OF MAGNESIUM, SODIUM, POTASSIUM AND CALCIUM FROM LAFLAMME LAKE WATERSHED.

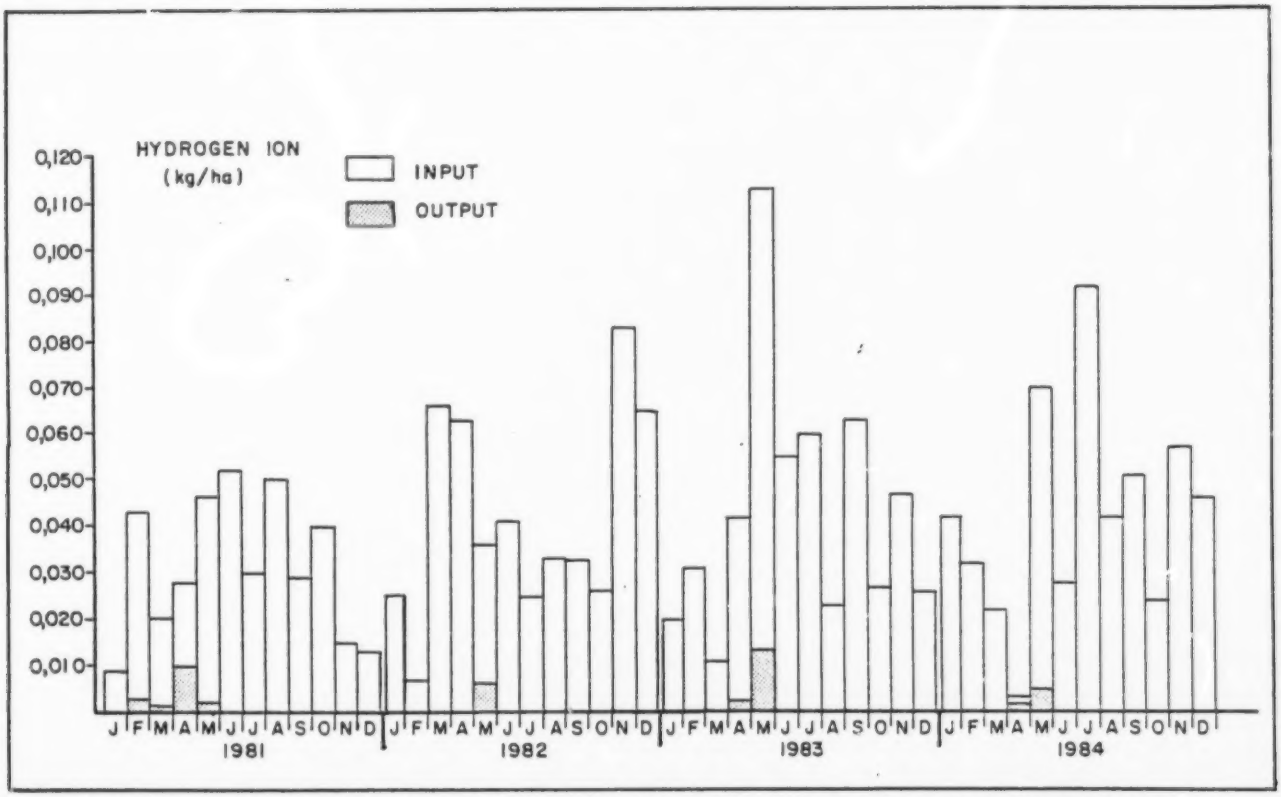

FIGURE 28: MONTHLY FLUX OF HYDROGEN ION FOR LAFLAMME LAKE WATERSHED.

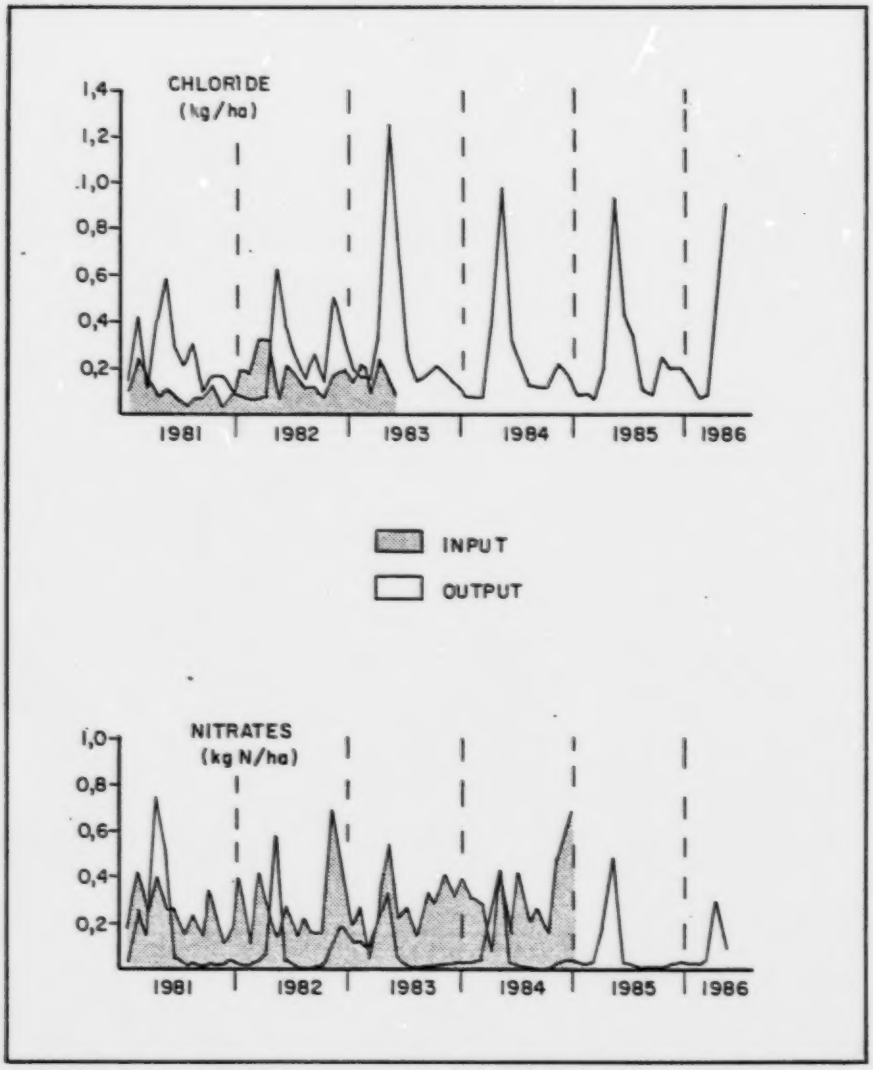

FIGURE 29 : MONTHLY FLUX OF CHLORIDE AND NITRATE FOR LAFLAMME LAKE WATERSHED.

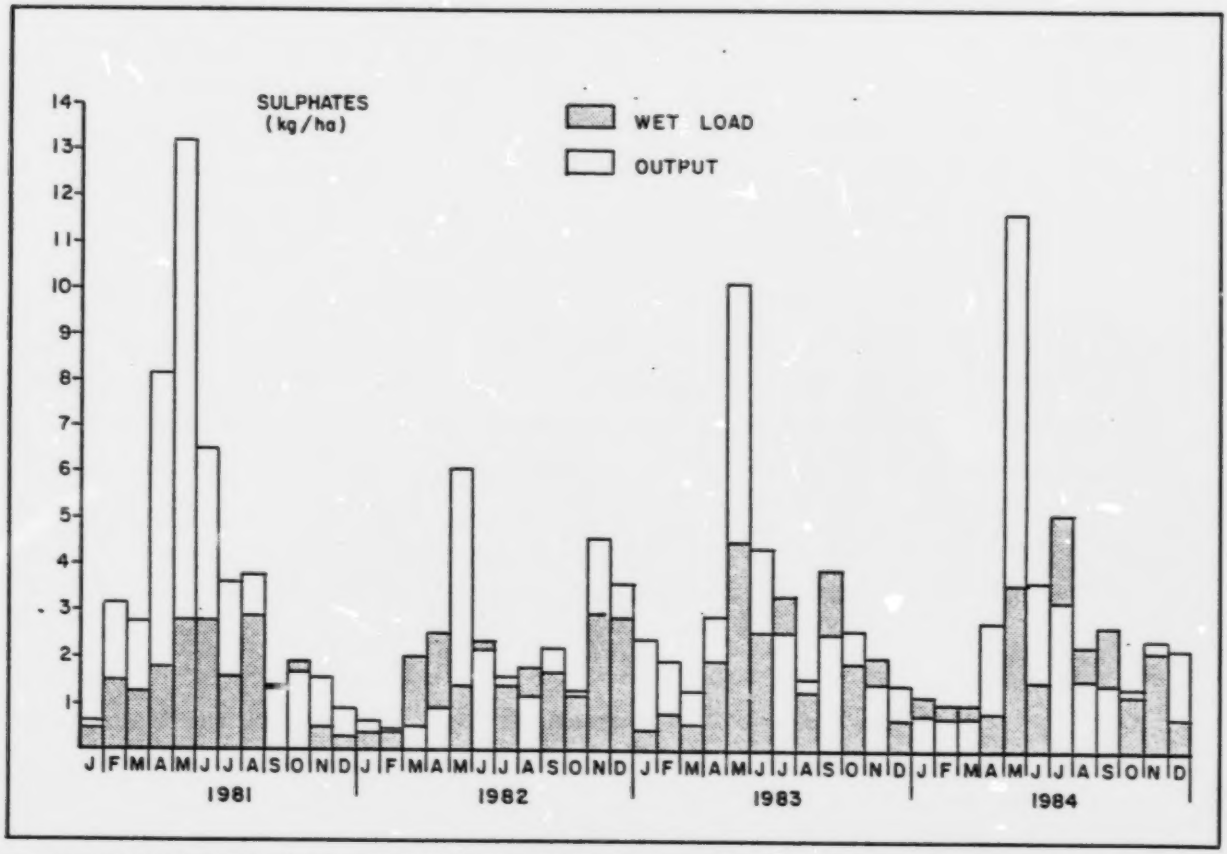

FIGURE 30: MONTHLY FLUX OF SULPHATES FOR LAFLAMME LAKE WATERSHED.

inputs are three times higher than output for nitrate ions, the accumulation of this ion in the snowpack and its release in the spring can lead to higher output than input in the month of May.

Sulphate and chloride ions are considered to be conservative meaning output should balance input. If so, the difference between wet atmospheric loading and output would be due to unmeasured atmospheric loading such as dry deposition. In the first two and a half years, chloride inputs exceeded outputs only during periods of snowpack build up, and atmospheric inputs represented only 47% of outflow. When CAPMoN data is considered, atmospheric input is 1,5 times outflow. There seems to be a serious problem with the consistency of input determinations in the case of the chloride ions.

When dry deposition estimates are added to atmospheric loading of sulphate ions, inputs balance outputs for the period considered (figure 31). However, the fit may not be as good for 1983 and 1984 or for the period before August 1981. There seems to be a large input of sulphate in May 1983 and 1984 which may not be a result of direct atmospheric loading. The pattern of monthly flux of sulphate does show periods when sulphates seem to be retained in parts of the system other than the snowpack. Sulphates could then be released in the spring from the soil or perhaps from decaying vegetation.

The contribution of groundwater in exporting material from the watershed can only be roughly estimated with some flow and chemistry data (Robitaille et al., 1983a). Chemistry data from two wells at 13 and 17 m below the surface were used for calculations. Water volume is considered to be 7% of incident precipitation. The estimates in table 31 are probably more representative of maximum outputs than actual ones, since no chemistry data was available for shallower flow in the area. For some parameters such as hydrogen, sulphate and chloride ions, groundwater outputs are low. For parameters that increase in concentration with residence time in surficial deposits (Ca, Mg, Na, K, Alk.), groundwater losses become important when compared to stream output.

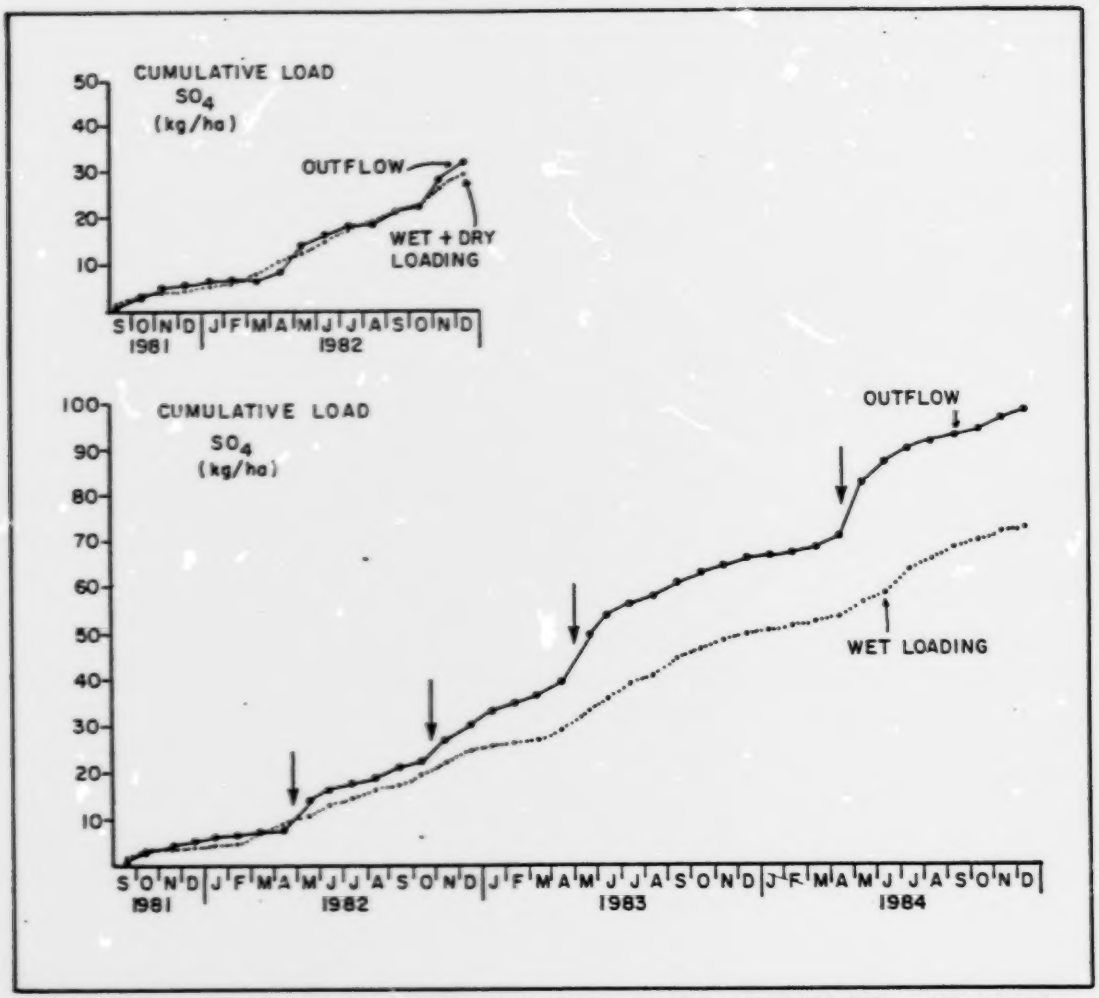
CUMULATIVE LOAD
SO_4
(kg/ha)
OUTFLOW
WET + DRY
LOADING
S O N D J F M A M J J A S O N D
1981
1982
CUMULATIVE LOAD
SO_4
(kg/ha)
OUTFLOW
WET LOADING
S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D
1981
1982
1983
1984

FIGURE 31 : CUMULATIVE INPUT AND OUTPUT OF SULPHATES FOR LAFLAMME LAKE WATERSHED.

Table 31. Atmospheric wet inputs, stream and groundwater outputs (kg/ha/yr).

Parameter	Atmospheric Wet Inputs (1981-84)	Stream Output June 81 - May 86	Estimated Groundwater Outputs
H	0,48	0,011	0,0002
SO_4	21,9	33,2	1,9
Cl	1,6	3,1	0,4
NO_3	3,3	0,9	0,2
Ca	1,5	15,9	4,0
Mg	0,2	3,3	2,0
Na	1,1	5,9	2,0
K	0,3	2,0	0,5
Alk		28,3	26

CONCLUSION

Laflamme Lake is a small headwater lake surrounded by a boreal forest ecosystem. It receives precipitations with an average pH of 4,4 and an average wet sulphate load of 22 kg/ha/yr. Dry deposition is believed to be close to 14% of total sulphate input. There exists a seasonal cycle in precipitation quality with higher concentrations of sulphate and hydrogen ions measured in the spring and summer. Atmospheric loading is episodic in nature and levels as high as 5 kg SO_4/ha were measured in July 1984.

Lake water composition is quite different and much less acidic than that of incident precipitation indicating the influence of watershed processes in determining lake water quality. A large portion of lake recharge occurs via groundwater flow. Biological activity, rates of flow and changes in seasons, caused pronounced annual cycles for many but not all parameters. Only very important inputs of precipitation caused noticeable changes in water quality due to atmospheric input alone. Such important inputs occur when water and pollutants accumulated in the snowpack are released in the spring. April and May contribute close to 40% of annual flow at the outlet. During this period, important dilutions occur for parameters with low concentrations in the snowpack (Ca, Mg, Na, conductivity). Decreases in alkalinity are even more pronounced, as part is used to neutralize the increases in acidity to the lake system. Nitrate, colour, potassium and heavy metal concentrations tend to be high in the spring. Because of the ice cover and the inverse thermal stratification, the acidic melt water tends to affect mostly the upper meter of the lake. When the ice cover disappears, the system recovers rapidly. The fall rains of 1982 also brought about the same type of changes in the system but at a smaller magnitude.

When looking at the complete data set, it is obvious that the first half of 1981 was a rather particular period for Laflamme Lake. An important rain event occurred in February and lead to a midwinter thaw. The pH and alkalinity depression resulting from this thaw and the subsequent spring melt were very pronounced and sulphate levels were unusually and even questionably high until June when they dropped to levels of 4 mg/l. The only reported fish mortality to date also occurred in 1981.

Since the summer of 1981, there have been increases in sulphate ion concentrations as well as in conductivity and heavy metal levels in surface waters. No significant trends have been seen for pH or alkalinity values. Paleolimnological cores also gave no indication of changes in pH over the time span covered by the sediment core. However, in the Quebec LRTAP network, all of the nine temporal stations with four years of bimonthly data show trends of decreasing pH (Haemmerli, 1987). Increases in sulphate concentrations were seen for lakes with low residence times (below 15 months).

Output of ions in streamflow basically reflects outflow patterns except for nitrate ions. The highest output for all parameters occurs in May when maximum outflow occurs. For the four years of available data, atmospheric inputs of hydrogen ions on a monthly basis were always higher than outputs. This means that the hydrogen ion is retained in the watershed. For other ions (Ca, Mg, Na, K) the watershed acts as a source of ions usually through weathering and inputs are always lower than outputs. Nitrate, chloride and sulphate ions had crossover patterns with periods of net accumulation in the watershed (snowpack, soil) and periods of net export. A more extended precipitation series will be required before investigating the effect of acid loading on the ion budget of the watershed.

Work in the field of long range transport is now shifting from an emphasis on understanding processes and refining a target loading to protect the aquatic environment, towards the regular and long term assessment of the efficacy of SO_2 emission reductions at Canadian and United States sources. Oxides of sulfur and nitrogens are now being viewed as only one aspect of air pollution in which oxidants, heavy metals and toxic organic substances can not be neglicted for long.

The use of calibrated watersheds may also be expanded in view of the growing concern about setting up an Environmental Monitoring Programm. This type of program, already in place in Sweden, uses a number of reference areas to monitor, detect and even expose the effects of environmental disturbances related to human acitivity on the terrestrial environment (soil, plants,

fauna), air, groundwater and on running waters. An important aspect of this approach is that environmental monitoring is considered as a constant and regular recording of the state of the environment rather than short-lived intense research efforts concentrated on one or two problems.

This growing concern about being able to detect and follow the effects of human activity on our surrounding environment is not only present in the scientific community but also in the general population. The appropriate tools to answer our questions must be put in place and/or maintained in the years to come.

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ANNEX

ANNEX . Monthly weighted concentrations of wet precipitation.

Date	pH	H mg/l	SO4 mg/l	NNO3 mg/l	Cl mg/l	Ca mg/l	NNH4 mg/l	Mg mg/l	Na mg/l	K mg/l
81 1	4,5	32,5	1,91	0,66	0,36	0,17	0,53	0,02	0,09	0,04
2	4,7	18,1	0,64	0,18	0,11	0,06	0,05	0,01	0,15	bl
3	4,6	22,4	1,43	0,29	0,16	0,07	0,19	0,01	0,17	0,02
4	4,6	22,6	1,42	0,32	0,06	0,24	0,19	0,03	0,08	0,02
5	4,4	37,4	2,25	0,21	0,09	0,12	0,17	0,02	0,13	0,03
6	4,6	27,0	1,46	0,14	bl	0,07	0,13	0,01	0,03	0,02
7	4,4	38,4	2,04	0,18	bl	0,10	0,16	0,01	0,09	0,02
8	4,6	26,3	1,52	0,13	bl	0,06	0,10	0,01	0,05	0,02
9	4,5	31,0	1,57	0,15	0,07	bl	0,14	0,01	0,04	0,02
10	4,4	36,1	1,70	0,30	0,10	0,10	0,14	0,01	0,04	0,02
11	4,5	31,6	1,09	0,21	0,06	0,07	0,02	0,01	0,12	0,04
82 1	(4,7	21,9	0,38	0,35	0,17	0,10	0,03	0,01	0,18	bl)
2	4,7	21,6	1,21	0,34	0,52	bl	0,02	0,01	0,18	bl
3	4,2	59,3	1,84	0,38	0,30	0,09	0,14	0,01	0,11	0,02
4	4,2	66,1	2,66	0,29	0,34	0,10	0,17	0,02	0,08	0,02
5	4,0	94,1	3,52	0,34	0,14	0,20	0,37	0,01	0,12	0,02
6	4,4	36,3	2,08	0,23	0,19	0,06	0,25	0,01	0,07	0,03
7	4,6	25,4	1,48	0,15	0,17	0,10	0,14	0,01	0,06	0,02
8	4,6	28,0	1,49	0,18	0,09	0,10	0,14	0,01	0,09	0,02
9	4,5	29,2	1,50	0,13	0,11	0,06	0,12	0,01	0,04	bl
10	4,3	45,8	2,05	0,28	0,12	0,05	0,21	0,01	0,06	0,02
11	4,4	42,7	1,55	0,35	0,09	bl	0,13	0,01	0,05	0,02
12	4,4	42,8	1,90	0,27	0,13	0,05	0,10	0,01	0,10	0,02
83 1	4,7	19,8	0,47	0,17	0,12	bl	0,04	0,01	0,04	bl
2	4,6	24,5	0,64	0,21	0,15	bl	0,05	0,01	0,04	0,02
3	5,0	10,9	0,55	0,05	0,09	bl	0,01	0,01	0,02	bl
4	4,7	21,7	0,99	0,10	0,12	bl	0,06	0,01	0,07	bl
5	4,3	46,5	1,86	0,23	0,06	0,09	0,16	0,01	0,03	0,02
6	4,1	72,7	3,44	0,28	0,11	0,07	0,36	0,01	0,05	0,03
7	4,4	43,0	2,42	0,20	0,21	0,13	0,23	0,02	(0,10)	0,04
8	4,5	34,2	1,89	0,19	0,41	0,21	0,20	0,03	-	0,02
9	4,4	36,2	2,23	0,19	(0,27)	0,15	0,25	0,02	-	0,03
10	(4,6)	(25,0)	(1,71)	0,25	(0,26)	0,20	0,22	0,03	(0,24)	0,04
11	4,5	28,2	1,26	0,26	(0,44)	0,30	0,16	0,02	(0,93)	0,02
12	4,8	14,7	0,36	0,16	(0,33)	0,08	(0,11)	0,01	-	0,02
84 1	4,1	88,2	2,48	0,83	(0,35)	0,05	0,32	0,01	-	0,03
2	4,5	34,0	1,06	0,31	(0,29)	0,07	(0,12)	0,01	-	0,02
3	4,4	36,6	1,70	0,41	(0,25)	0,26	0,13	0,04	-	0,03
4	5,3	4,5	1,04	0,09	0,51	0,36	(0,31)	0,08	(0,60)	(0,04)
5	4,3	47,3	2,42	0,26	(0,28)	0,28	0,25	0,04	-	0,04
6	4,5	30,9	1,61	0,16	(0,24)	(0,20)	0,14	0,02	-	0,04
7	4,2	62,1	3,44	0,28	(0,27)	(0,30)	0,22	0,02	-	0,03
8	4,4	42,8	2,33	0,20	(0,35)	(0,23)	0,27	0,01	-	0,03
9	4,3	49,2	2,57	0,26	(0,21)	(0,19)	0,26	0,01	-	0,02
10	4,3	45,9	2,30	0,26	(0,22)	0,06	0,16	0,01	(0,39)	0,02
11	4,3	45,3	1,71	0,39	(0,36)	0,06	0,15	0,02	-	0,01
12	4,4	38,9	0,64	0,52	0,07	0,05	0,05	0,01	0,05	0,01

bl : below detection limit ( ) less than 50 % of volume analyzed.